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The Sorption of Gases
and Vapours by Solids

TWENTIETH-CENTURY CHEMISTRY

Edited by J. C. PHILIP, F.R.S.

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THE SORPTION OF GASES AND VAPOURS BY SOLIDS

BY

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WITH 151 DIAGRAMS

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PREFACE

The publication of this monograph on sorption was inspired by an invitation to give a series of Special Lectures at the University College of Wales. The public lectures were given in October, 1928, at Aberystwyth under the caption, "Sorption: Interactions at Surfaces, Constituting a Distinctive Field of Science." In presenting the material to a wider audience, it seemed worth while to collate as much as possible of the existing evidence, more especially because the literature upon this important subject has never been systematically assembled.

Some years of work have gone to the task, although this volume is confined to a discussion of the sorption of gases and vapours. Much material has been collected towards a survey of the even larger subjects of sorption of liquids and solutions, and of sorption in liquid interfaces with their more immediately practical and their intrinsically interesting and varied phenomena.

It is hoped that the extensive bibliographies, which list authors and the materials which they have studied, will be of substantial assistance to those interested in this rapidly extending science. As a rule, authors in this field do not refer to the work of others who have done similar work on similar materials. Scientific contributions in the general literature may be partly appraised as much by the significance and quality of the relevant information which is left out as by that which is quoted.

Reference may be made to the following treatises which deal more or less extensively with the subjects here treated. H. Freundlich, *Kapillarchemie*, Bd. I, pp. 143-217 (Akademische Verlagsgesellschaft, m.b.H., Leipzig, 1930); the excellent brochure by O. Blüh and N. Stark, *Die Adsorption*,

Sammlung Vieweg, Heft 93 (F. Vieweg und Sohn, Braunschweig, 1929); and the parallel monograph by E. Hückel, *Adsorption und Kapillarkondensation* (Akademische Verlagsgesellschaft, m.b.H., Leipzig, 1928); W. D. Bancroft, *Applied Colloid Chemistry* (McGraw-Hill Book Co., New York, 1926); E. K. Rideal, *An Introduction to Surface Chemistry*, pp. 168–252 (University Press, Cambridge, 1930); together with other compilations to which attention is called at appropriate places in the text. A manual dealing with the routine testing and the technical applications of sorbing materials has been supplied by F. Krczil, *Untersuchung und Bewertung technischer Adsorptionsstoffe* (Akademische Verlagsgesellschaft, m.b.H., Leipzig, 1931).

It should be emphasized that absolute measurements of sorption and its phenomena demand not merely the exacting carefulness of precision measurements in chemistry or physics, but, above all, the most rigorous control of the chemical nature and physical state of the surface. This becomes evident from the reflection that chemicals of the highest purity are wholly changed in sorptive properties if only the surface to the depth of a few Ångstrom units has suffered alteration. Such work has seldom been attempted. It will become evident when reading through the fairly complete account of the existing data that nearly all will ultimately have to be superseded by much more careful investigations. The author will be gratified if the criticisms, implicit and explicit, which he has ventured to make may be taken as helping towards this constructive work by learning from the experience of the past.

On the other hand, much of the older work must be remembered as an enduring achievement because it portrays the behaviour of materials as they commonly occur. Every reader must concede the value of the work of some of the earlier masters and will agree that many more recent investigations would have benefited if the earlier findings had not been so largely forgotten. The ever-increasing rate at which papers upon the subject of sorption are appearing not only testifies to the increased recognition of the importance of sorption and its applications but also strongly tempts many

of us to trust to a reference to the most recent papers for a knowledge of the subject. This procedure, when widely followed, soon leads to a superficial or even unsound development of theory and practice. The author has therefore taken great pains to lighten the labours of other students by compiling with especial care all that appears to be of permanent value in the existing literature.

The author will be very grateful if any of the numerous points which must have been overlooked are called to his attention, so that if a subsequent edition is published, it may become the source book that the author desires to create for the service of other investigators.

It should be noted that, in general, the abbreviations for literature references are those used by the Chemical Abstracts of the American Chemical Society.

The author is greatly indebted to his wife and Miss Margaret D. McDowell for their skilled assistance, and in particular to the latter for the care with which all accessible references were verified and for the preparation of the index of authors and of substances. The author also wishes to express his thanks to the following societies, journals and publishers for permission to reproduce certain diagrams and tables: The American Chemical Society, The Royal Society, The Chemical Society, The Society of Chemical Industry, The National Academy of Sciences, The London, Edinburgh and Dublin *Philosophical Magazine and Journal of Science*, *Chemical and Metallurgical Engineering*, *The Physical Review*, O. Spamer Verlag and Akademische Verlagsgesellschaft m.b.H. An exact reference has been made in the text to these and other citations.

Finally, the author would express special thanks to the Directors of Research of the British Cotton Industry Research Association, the British Silk Research Association, the Wool Industries Research Association, the Linen Industry Research Association and the Research Association of the British Rubber Manufacturers for having supplied, while the work was in the press, exhaustive literature references in regard to these subjects, together with original or unpublished data.

CONTENTS

	PAGE
PREFACE	V

PART I.—INTRODUCTORY

CHAP.

I	HISTORICAL AND GENERAL	I
	The classical sorption isotherm—Reversible equilibrium—Time—Temperature—Sorbing agents—Sorption from solutions—Practical importance	
II	METHODS OF MEASUREMENT AND EVALUATION OF THE RESULTS	17
	Standard method—Sorption balances—Sorption of mixtures—Sorption pipette—Dynamic methods—The optical method—Sorption of solutions—Precautions—Calculation	

PART II.—THE EXPERIMENTAL DATA

III	GENERAL BEHAVIOUR	33
	Significance of the formulæ describing sorption—Sorption at low pressures—Isobars and isosteres—Steric hindrance in sorption—Influence of temperature—Effect of time upon the various factors involved in sorption—Rate of sorption—Relation of amount of sorption to physical constants	
IV	SORPTION BY CHARCOAL	58
	“Active” charcoal—“Density” of charcoal—The importance of preliminary evacuation—Sorption of gases—Effect of high pressures—Sorption of carbon dioxide and ammonia—Sorption of chlorine, oxygen and oxides of nitrogen—Sorption of vapours—Summary—Sorption of water—Sorption of mercury vapour—Sorption of noble gases—Sorption of mixtures	
V	SORPTION BY CHABASITE, OTHER ZEOLITES AND PERMEABLE CRYSTALS	167
	The nature of zeolites—Molecular sieves and per-sorption—Sorption of water and other vapours—Siloxene	

CHAP.		PAGE
VI	SORPTION BY SILICA, POROUS RIGID JELLIES AND OXIDES	177
	Comparative behaviour of silica and charcoal—Silicic acid jelly and its dehydration—Effect of presence of air—Chemosorption or hydrates?—Jellies with other liquids—Isotherms with silica gel and other materials—Sorption of gases and vapours by silica gel—Other porous oxides—Practical significance of humidity changes	
VII	SORPTION BY GLASS	212
	The universal corrosion of glass surfaces—Permeability of glass and solubility therein—Greasy films upon glass surfaces—Sorption of water—Sorption of water on glass surfaces of supposedly known area—Sorption of other substances on glass surfaces of supposedly known area—Sorption of carbon dioxide and other soluble corrosive gases—Sorption of vapours	
VIII	SORPTION BY IMPERMEABLE CRYSTALS	246
	Sorption of water vapour by quartz and feldspar—Sorption of gases and water vapour by mica—Sorption of air and water vapour by sodium chloride—Sorption by calcium fluoride—Sorption by sugar	
IX	SORPTION BY METALS	259
	Occlusion and diffusion of gases in metals—The activation or electrification of desorbed gases—Adsorption on liquid mercury—Sorption by platinum and other noble metals—Sorption of hydrogen by palladium—Sorption of water and other vapours on smooth metallic surfaces—Sorption of gases by amorphous iron, nickel, copper and other catalysts—Sorption by alkali and alkaline earth metals—Reflection of electrons from metallic surfaces	
X	THE THICKNESS OF ADSORBED FILMS; AND THE AREA OF "SMOOTH" SURFACES AND POROUS BODIES	325
	Monomolecular, multilayer and classical thick films—Review of results in Chapters VII, VIII and IX—Methods of estimating areas: (a) Sorption of radioactive elements; (b) Sorption of dyes; (c) Rate of chemical attack; (d) Polarization during electrolysis; (e) Interference colours; (f) Rate of vaporization; (g) Assumption that the sorption of water measures the total area of the pores in charcoal; (h) Heat of wetting; (i) Bends in curves for porous bodies—Thickness of films and range of molecular attraction: (a) Insoluble films; (b) Liquid films; (c) Thick gaseous films	

CONTENTS

xi

CHAP.	PAGE
XI MOBILITY IN SORBED FILMS	352
Mobility of the outside layer of a crystal—Mobility upon glass surfaces—Relation to chemical reaction, catalysis and crystallization	
XII SORPTION BY CELLULOSE DERIVATIVES AND OTHER NON-RIGID GELS AND JELLIES	358
Swelling—Structure—Sorption of water by cellulose—Sorption by nitrocotton—Starch—Wool—Proteins—Rubber—Various materials	
XIII THE EFFECT OF SORPTION UPON THE SOLID	390
Distention of charcoal caused by sorption—Other related effects with various solids—Examples of disintegration and swelling caused by sorption—Effect of gases upon the properties of iron and platinum—Effect of hydrogen upon the dimensions and conductivity of palladium	
XIV HEAT OF SORPTION	400
Method of measurement—Typical heats of sorption—Comparison with heats of compression and with heats of reaction—Relations to the chemicals involved—Heats for water and mercury—Errors in initial heats of sorption—Sorption of oxygen by charcoal—Heats of sorption on metals—Compilations of heats of sorption and heats of wetting	
PART III.—HYPOTHESES AND THEORY OF SORPTION	
XV A BRIEF CLASSIFICATION OF SORPTION HYPOTHESES	427
XVI CAPILLARY CONDENSATION	432
Dependence of condensation in capillaries upon vapour pressure—Test of the constancy of pore volume deduced—The very low values deduced for capillary radii—Other evidence against condensation as a general explanation of sorption—Cases where capillary condensation undoubtedly occurs in addition to sorption—Influence of the neighbourhood of surfaces upon liquids	
XVII THE CLASSICAL HYPOTHESIS OF A THICK COMPRESSED FILM	447
Quantitative formulation of the compressed film hypothesis—Characteristic curve of adsorption—Relation between adsorption potential and van der Waals' constant a —Recent developments and modifications of the compressed film theory—Experimental disproof of the compressed film hypotheses for the case of highly porous bodies such as charcoal—Discrepancies in the compressed film hypothesis	

CHAP.		PAGE
XVIII	MONOMOLECULAR ADSORPTION	464
	Adsorption the result of the time lag between condensation and evaporation of molecules striking a surface—Langmuir's quantitative formulation—General applicability of the Langmuir theory—Significance of Langmuir terms in relation to other quantities—Change of maximum sorption with temperature—Multiple adsorption of a molecule on more than one atom of the solid—The formulation of Williams and Henry—Extension to the theory of surface films—Laminated or enchainned multimolecular films—General conclusions	
XIX	EVIDENCE FROM CONTACT CATALYSIS AS TO THE NATURE OF SORPTION	498
	Effect of the conception of monomolecular adsorption—The mechanism of the oxidation of carbon monoxide on platinum surfaces—Active patches or centres—Adlineation—Heats of sorption, activation and rate—Promoters	
XX	ELECTRICAL INTERPRETATION OF SORPTION	511
	Forces at present recognized—Definition and characterization of dipoles—Analysis of forces at a crystal surface—The concept of mirrored dipoles and mirrored quadrupoles—Mutual polarization of sorbed molecules—Other dielectric relations	
	AUTHOR INDEX	529
	SUBSTANCE INDEX	554
	SUBJECT INDEX	574

PART I

INTRODUCTORY

CHAPTER I

HISTORICAL AND GENERAL

Sorption is as old as the greater part of chemistry itself, its phenomena being first mentioned by C. W. Scheele ¹ in a letter to P. J. Gahn on March 1, 1773, describing experiments on gases exposed to charcoal. The Abbé F. Fontana ² described in 1777 an experiment which is still commonly shown in lecture demonstrations.³ Glowing charcoal is plunged under mercury and allowed to rise into an inverted tube containing gas, whereupon the whole or the greater part of the gas disappears. It is sorbed (**sorbeo**, to suck in) by the charcoal.^{4,5} Lowitz,⁶ in 1785, when preparing pure tar-

¹ See also C. W. Scheele, *Chemische Abhandlung von der Luft und dem Feuer*, 1777. Hrsg. von Wilhelm Ostwald, Leipzig, 1894 (Ostwald's *Klassiker der exakten Wissenschaften*, No. 58).

² F. Fontana, *Mem. Mat. Fis. Soc. Ital.*, 1777, **1**, 679.

³ For a series of ingenious and striking lecture demonstrations see J. Dewar, *Proc. Roy. Inst. Gt. Brit.*, 1905-07, **18**, 177, 443, 747.

⁴ The term "occlusion" was suggested by Graham to signify the absorption of or shutting up of gases in solid substances; it thus has the same meaning as the term sorption and it is now chiefly used in connexion with the behaviour of gases and metals (T. Graham, *Phil. Trans. Roy. Soc.*, London, 1866, **156**, 399; see also *Chem. and Phys. Researches*, 1876, p. 263).

⁵ A brief account of the earlier work on this subject is given by Wilhelm Ostwald (*Lehrbuch der allgem. Chem.*, 2 Aufl., 1891, **1**, 1084; 2 Aufl., 1906, 2, Abt. 3, 217; also *Klassiker der exakten Wissenschaften*, No. 58, 1894).

⁶ T. Lowitz, *Crell's Chem. Ann.*, 1786, **1**, 211; 1788, **2**, 36, 131. P. Figuier (cf. L. Figuier, *Mon. sci.*, (4), 1895, **9**, 5) discovered the decolorizing power of bone charcoal and its regeneration on ignition.

taric acid, observed that charcoal likewise takes up colouring matter from solutions.

Sorption was naturally investigated by all the early masters such as Priestley,¹ de Morveau,² and Morozzo,³ who approached it without any strong chemical preconceptions. Many features of our present knowledge are outlined in the systematic investigation of de Saussure in 1814.⁴ He found, for instance, that all sorts of gases are taken up by all sorts of porous bodies, such as meerschaum, wood, asbestos, mountain cork and charcoal, that heat is evolved in the process, and that the most readily condensible gases are most readily taken up. This is exemplified by the data in table 1, which shows some of de Saussure's results, together with some of the later data of Hunter,⁵ using the same method, and which adduces, for comparison, the boiling points of the various substances in the liquefied condition. It should be noted that the volume of the charcoal is its external or apparent volume, including any pores.

TABLE I

The number of Volumes of various Gases and Vapours taken up by one Volume of Charcoal at ordinary Temperature and Pressure

	Boxwood de Saussure	Coconut Hunter	Boiling point of Liquid
Ammonia	90	172	— 35·5°
Hydrochloric acid . .	85	—	— 82·9°
Sulphurous acid . . .	65	—	— 10°
Sulphuretted hydrogen .	55	—	— 60·2°
Nitrous oxide	40	85	— 89·8°
Carbonic acid gas . . .	35	68	(— 79°)
Olefiant gas C ₂ H ₄ . . .	35	75	— 105°
Carbonic oxide	9·4	21	— 190°
Oxygen	9·3	18	— 182·8°
Nitrogen	7·5	15	— 195·7°
Hydrogen	1·75	4	— 252·6°

¹ J. Priestley, *Experiments and Observations on Different Kinds of Air*, London, 1790, **1**, 129.

² L. B. G. de Morveau, *Nouv. Mém. Acad.*, Dijon, 1782, p. 30.

³ C. L. Morozzo, *Obs. Phys.*, 1783, **22**, 294; 1783, **23**, 362.

⁴ T. de Saussure, *Gilbert's Ann. der Physik*, 1814, **47**, 113; *Ann. Phil.*, 1815, **6**, 241, 331.

⁵ J. Hunter, *J. Chem. Soc.*, 1872, **25**, 649; *Phil. Mag.*, (4), 1865, **29**, 116.

de Saussure also observed such phenomena as that charcoal continues to take up oxygen for an indefinite period.¹ He is the author of the classical explanation of sorption that is now commonly known as the Polányi or compressed film hypothesis (see Chapter XVII); this is still held in some quarters up to the present day.

But this was at a stage of the development of chemistry when, after a famous controversy, the constancy of chemical composition had finally been established, and such things as the principle of mass action and sorption, which did not readily square with it, were ignored for generations. In fact, in both cases it was not until the 'sixties that anyone made further observations worthy of note.²

These phenomena found employment only in industrial processes where theoretical conceptions were not kept in the foreground. Apart from deodorizing and decolorizing with charcoal,³ pure chemists rarely made use of them, an exception

¹ For more recent work see H. H. Lowry and G. A. Hulett, *J. Am. Chem. Soc.*, 1920, **42**, 1408, and Chapter IV, pages 120 and 121.

² See, however, the important paper of M. E. Mitscherlich, *Taylor's Scientific Memoirs*, 1846, **4**, 1 (from *Ann. chim. phys.*, (3), 1843, **7**, 15).

³ E. Filhol (*Compt. rend.*, 1852, **34**, 247) gives an instructive table of amount of colour taken up by various substances in comparison with charcoal. J. Stenhouse (*Pharm. J. Trans.*, 1854, **13**, 454) used charcoal in a respirator as a deodorant. E. C. C. Stanford (*J. Chem. Soc.*, 1873, **26**, 14; *Chem. News*, 1872, **26**, 237) showed that charcoal decolorizes and deodorizes without oxidizing nitrogenous matter. See also P. Cazeneuve (*Compt. rend.*, 1890, **110**, 788), who shows loss of decolorizing power of animal chars on heating in a stream of nitrogen. Filhol gives the following interesting table of the quantities of tincture of litmus and of solution of sodium sulphindigodate which are decolorized by equal amounts of various powders, bone black being taken as 100 :

	Litmus	Sulphindigodate
Bone black	100	100
Iron reduced by H ₂	95	100
Ferric hydroxide	129	2
Alumina	116	10
Calcium phosphate	109	2
Precipitated PbS	130	17
Manganese dioxide	89	14
Indigo	80	14
Zinc oxide	80	7
Stannic acid	70	0

being the application of sorption by charcoal and subsequent extraction in alcohol, which Graham and Hofmann ¹ employed in 1853 in order to demonstrate the presence of strychnine in certain samples of beer. Nevertheless, it is now recognized that sorption occurs well nigh universally. Wherever there is a solid or liquid surface, there is sorption. The mass of observations on this subject is now growing at the rate of more than one paper in the scientific literature each day.

With the rise of physical and theoretical chemistry as a distinctive aspect of the science during the last fifteen or twenty years of the nineteenth century, there was a recrudescence of interest in these long neglected phenomena, and when the thermodynamic theories of Gibbs and especially van't Hoff led to a successful quantitative formulation of chemical action—mass law, phase rule, solubility, distribution ratio, etc.—the attempt was made to apply the new knowledge to cases of sorption. The first suggestion towards employing the mass law was to try to get a proportionality between the pressure of the gas, or the concentration of the solution, and the concentration in the solid. Thus if x grams of substance are sorbed by m grams of solid, proportionality would be represented by the equation, $x/m = kp$ or kc , where p and c represent the pressure of the gas or the concentration of the solution. Or if association had to be taken into account, p and c could be raised to some integral power. This was the path followed, for example, by Küster ² in his study of the distribution of iodine between aqueous solution and starch, and by Walker and Appleyard ³ when investigating the dyeing of silks with picric acid.

	Litmus	Sulphindigodate
Lead chromate	70	2
Litharge	67	4
Antimony oxide	67	2
Antimony sulphide . . .	59	0
Lead sulphate	50	14
Precipitated BaSO ₄ . . .	50	0
Colloidal sulphur	27	0
Copper oxide	27	0
Calomel	22	0

¹ T. Graham and A. W. Hofmann, *J. Chem. Soc.*, 1853, **5**, 173.

² F. W. Küster, *Liebig's Ann. der Chem.*, 1894, **283**, 360.

³ J. Walker and J. R. Appleyard, *J. Chem. Soc.*, 1896, **69**, 1334.

THE CLASSICAL SORPTION ISOTHERM

As a matter of fact it was found that the observations corresponded to a modified formula, $x/m = kp^{1/n}$ or $x/m = kc^{1/n}$, where $1/n$, however, instead of being an integer, is any sort of irrational fraction varying with circumstances between 1 and $1/10$, and is frequently in the neighbourhood of $1/3$. Thus for picric acid, $1/n$ was $1/2.7$, and for starch, about $1/10$.

This is the famous "exponential"¹ (really parabolic) formula which is still the best summarized description of the approximate quantitative behaviour of the extraordinarily diverse instances of sorption.² Such instances range from the sorption of argon at temperatures of liquid air to the gases evolved from molten glass or to the mercury sorbed even by heated carbon; from the complicated phenomena

¹ The usual custom of calling this the "Freundlich exponential isotherm" is amusing, because it is neither exponential nor in any way due to Freundlich, who, as a matter of fact, in his first big paper on adsorption, attacked and rejected it in favour of another empirical formula proposed by K. Kroeker, *Dissert.*, Berlin, 1892 (see H. Freundlich, *Habilitationsschrift*, Leipzig, 1906; reprinted in *Z. physik. Chem.*, 1906, **57**, 385. See also, H. Freundlich and G. Losev, *Z. physik. Chem.*, 1907, **59**, 284. Cf. J. W. McBain, *J. Chem. Soc.*, 1907, **91**, 1683). Another variant in colloidal treatment is to call this the Boedecker formula (Wo. Ostwald and R. de Izaguirre, *Kolloid-Z.*, 1922, **30**, 280; H. Sallinger, *Kolloidchem. Beihefte*, 1927, **25**, 402), because C. Boedecker (*J. für Landwirtschaft*, 1859, **7**, 48) stated that sorption by soil was proportional to the square root of the *initial*, not the equilibrium, concentration. J. M. van Bemmelen (*Mitteilungen der Landwirtschaftlichen Versuchsstationen*, 1888, **35**; *Die Absorption*, Dresden, 1910, p. 110) pointed out Boedecker's mistake and noted that in his own results the amount of sulphuric acid sorbed by metastannic acid was approximately proportional to the fifth root of the equilibrium concentration. Possibly we might have called our equation the van Bemmelen formula had he not added that such formulæ were worthless.

² It will be shown later that it is definitely untrue if applied over the whole range of sorption of a gas or vapour by a solid, but it serves as a rough approximation over a middle range. The Langmuir formula, $\frac{x}{m} = \frac{abp}{1+ap}$, where a and b are constants and p is the pressure, is a much more exact formulation for gases and vapours.

observed in the dyehouse to the use of the gas mask in chemical warfare; from the reactions of soil chemistry to many of those observed in living cells. Indeed, now that we have given this subject a definite position in chemical science, we find that it is of almost universal occurrence, being manifest at almost every surface of separation. We readily admit its widespread existence now that we realize that the world with which we have to deal consists to only a small extent of crystalline chemicals. Most substances in which we are interested and with which we have to do in daily life are in the colloidal condition, of which the distinctive feature is the enormous relative development of surfaces owing to the fine state of subdivision into colloidal particles.

The action of porous bodies upon gases was the first example to be recognized, and it is also that which lent itself most readily to theoretical treatment. Take, for instance, the effect of charcoal at the temperature of liquid air upon hydrogen; ¹ the amount of hydrogen taken up is proportional to the cube root of the pressure. This quantitative behaviour is incompatible with the formulation of chemical reaction of any sort, homogeneous or heterogeneous, for in such cases we should have the process governed by the mass law or the phase rule. Nor, indeed, is it possible to regard hydrogen as being dissolved in the charcoal in the form of solid solution, that is, **a**bsorption, since this would necessitate the impossible conclusion that the dissolved hydrogen had a molecular weight two-thirds of that of the single hydrogen atoms themselves. Similarly, in the case of iodine sorbed by starch from solution, the amount of iodine in the starch is proportional to the 1/10 root of the concentration of the solution, and if this were interpreted as a mere distribution or mass action equilibrium, it would entail the assumption that each atom of iodine in the starch had dissociated into five parts. It is therefore seen how distinctive is the ordinary sorption formula, $x/m = kp^{1/n}$.

¹ M. W. Travers, *Proc. Roy. Soc. (London)*, A, 1906, **78**, 9; J. W. McBain, *Phil. Mag.* (6), 1909, **18**, 916; *Z. physik. Chem.*, 1909, **68**, 471.

REVERSIBLE EQUILIBRIUM

It might be objected that the peculiar form of this equation was due to our not working with anything definite, that is, with equilibrium conditions, but in every case investigated, it is found that as a matter of fact the results observed represent true reversible equilibria. One might infer this from the fact that only a few seconds are required for the greater part of any gas to be taken up, this being the case with even such an inert gas as argon when sorbed by charcoal at the temperature of liquid air. The best way of proving this, however, is to compare the amount of sorption in two experiments carried out under similar conditions but in one of which an excess of gas is allowed to be taken up by a short exposure to a high pressure so that equilibrium is approached from both sides, that of supersaturation and of under-saturation.¹ It is found that precisely the same condition is attained in the two cases. Indeed this is very general, whether in the case of gases or solutions, provided that the experiments are carried out in a definite time. Joulin even found that when several gases were added, the final result was independent of the order in which they were added. Obviously the distinctive feature here is the rapid equilibrium on the surface, that is, true adsorption (the term is due to E. du Bois-Reymond ²) ; in other words, surface condensation which will have to be described in greater detail later.

TIME

Now it is found that in spite of this initial equilibrium, further amounts of gas are taken up over long periods of time,

¹ L. Joulin, *Ann. chim. phys.*, (5), 1881, **22**, 398.

² See H. Kayser, *Wied. Ann. der Physik*, 1881, **14**, 451. The general phenomena of the taking up of gases by liquids and solids were designated "absorption" a century ago (compare J. S. T. Gehler, *Phys. Wörterbuch*, Leipzig, 1825, **1**, 40). Hence M. L. Frankenheim (*Die Lehre von der Cohäsion*, Breslau, 1835, p. 158) proposed the term "insorption" for solution and "adsorption" for intimate mixing as in pores or upon surfaces, without solution. These terms were long since forgotten and the word adsorption was coined afresh.

obviously by processes of diffusion, absorption, or solid solution. Some of the author's experiments with carbon and solutions of iodine lasted as long as eleven years, during which time the amount of sorption was doubled without any evidence of chemical reaction having taken place.¹ In many cases, on the other hand, it can be shown, as, for instance, in the case of oxygen and charcoal, that a slow chemical reaction is occurring which may go on almost indefinitely. It is for these reasons that the author ventured in 1909² to propose the truncated expression "sorption" as a non-hypothetical term to denote all cases involving more than one of these factors and to include every case which had not yet received sufficient study to prove that adsorption alone occurred. Even where the effect is confined to the surface, there may be a number of such factors involved, chemical and electrical effects, surface tension, hydrolysis, double decomposition, formation of colloidal and solid films.

"The author wishes to make it quite clear that the standpoint here presented is by no means that all cases of sorption are of composite type; but rather that until any particular case has received adequate experimental investigation it should be referred to as sorption and not given the more definite and therefore hypothetical name of adsorption, absorption, chemical reaction, etc. These names should be restricted to cases in which it has been proven to consist of only one of these."³

¹ J. W. McBain, *Trans. Farad. Soc.*, 1919, **14**, 202.

² J. W. McBain, *Z. physik. Chem.*, 1909, **68**, 471; *Phil. Mag.*, (6), 1909, **18**, 916. For further evidence for the case of hydrogen and carbon see J. B. Firth (*Z. physik. Chem.*, 1914, **86**, 294). Again, the careful investigation of the occlusion of hydrogen by palladium has been shown to belong to this composite type (A. Holt, E. C. Edgar and J. B. Firth, *Z. physik. Chem.*, 1913, **82**, 513; 1913, **83**, 507; A. Sieverts, *Z. physik. Chem.*, 1914, **88**, 103; G. Wolf, *Z. physik. Chem.*, 1914, **87**, 575; A. Holt, *Proc. Roy. Soc. (London)*, A, 1914, **90**, 226). Georgievics has published much evidence in the cases of dissolved substances sorbed by textiles; Langmuir is led to the same conclusion in discussing the time relationships of the sorption of water vapour by glass or silica, etc.

³ J. W. McBain, *Trans. Farad. Soc.*, 1919, **14**, 203.

TEMPERATURE

Even mere change of temperature may change the very nature of the sorption observed. For example, in Dewar's work at low temperatures, oxygen is sorbed by charcoal in the same reversible fashion as nitrogen, and to about the same extent, and with a similar evolution of heat. Both gases may be largely removed from the charcoal by evacuation.¹ Calvert² found that between 0° and 150° C. the oxygen sorbed on charcoal is not readily recovered but has the power of oxidizing ethyl alcohol to acetic acid, and ethylene to carbon dioxide and water. At higher temperatures, very little oxygen is recovered as such on evacuation; the gas removed is largely a mixture of carbon monoxide and carbon dioxide.³ This change is expressed by saying that at low

¹ J. Dewar, *Proc. Roy. Soc. (London)*, 1904, **74**, 127; *Proc. Roy. Inst. Gr. Brit.*, 1905, **18**, 184. M. S. Shah (*J. Chem. Soc.*, **1929**, 2670, 2685) showed that of 535 c.c. of oxygen sorbed at -190°C. , 522 c.c. could be pumped off with a "Hyvac" oil-pump at -78°C. At 0°, of 152.4 c.c. sorbed, 133.5 c.c. could be pumped off at 0.011 mm. Hg at 0° C.; upon long continued evacuation during successive increments of temperature, no more oxygen was obtained and only 2.1 c.c., mostly carbon dioxide, up to 280°. At 300° carbon monoxide began to appear and above 750° it was no longer accompanied by carbon dioxide. The total gas finally obtained up to 950° C. was 179.7 c.c. Gases were measured in all cases at N.T.P. H. H. Lowry and G. A. Hulett (*J. Am. Chem. Soc.*, 1920, **42**, 1411) found at 25° C. that about one-half the oxygen sorbed by activated coconut charcoal and by German gas-mask charcoal could be recovered as such; a far larger proportion could be recovered from English gas-mask charcoal. See also Chapter IV, pages 69 and 121; also J. Boehm, *Botan. Ztg.*, 1883, **41**, 521, 537, 553.

² F. C. Calvert, *J. Chem. Soc.*, 1867, **20**, 293; also J. B. Firth, *Trans. Farad. Soc.*, 1924, **20**, 370. It is of common occurrence that gases which are non-reactive at ordinary conditions react with great readiness when sorbed. One illustration may be cited; namely, hydrogen in palladium, which reduces a solution of mercuric chloride, ferric salt or a ferricyanide and unites with chlorine and iodine in the dark. It is as much more reactive than hydrogen as ozone is in comparison with oxygen (T. Graham, *J. Chem. Soc.*, 1869, **22**, 432; *Chem. Zentr.*, 1867, **38**, 134).

³ R. A. Smith, *Proc. Roy. Soc. (London)*, 1863, **12**, 424; C. J. Baker, *J. Chem. Soc.*, 1887, **51**, 249; H. B. Baker, *Phil. Trans. Roy. Soc.*

temperatures, the sorption is of the "physical" type, whereas at higher ones, it may be called "chemisorption";¹ the distinction may or may not be fundamental, and both types may well be subject to the same general laws, but no purely physical explanation can account for both. The importance of careful scrutiny of any physical theory is that if true it must be general and must be operative even in the presence of chemical effects.

In general, sorption is most prominent at low temperatures. Advantage was taken of this by Dewar and Tait² as early as 1874 in producing vacua by means of charcoal. Later, the use of liquid air made this a highly efficient means of producing high vacua. Dewar³ in 1905 showed that at sufficiently low temperatures even helium is sorbed by charcoal in as large amounts as are other substances at more common temperatures. Such are the regularities in the behaviour of sorption that he was even able to predict the boiling point of liquid helium from these observations, although helium had not yet been liquefied; his estimate was between 5° and 6° absolute, whereas it has now been observed and is 4.4° absolute.

The effect of temperature on the sorption of gases and vapours is well illustrated by the curves for the sorption of carbon dioxide by charcoal at various temperatures. These

(London), A, 1888, **179**, 571; T. F. E. Rhead and R. V. Wheeler, *J. Chem. Soc.*, 1913, **103**, 461; S. McLean, *Trans. Roy. Soc. Canada*, (3), 1921, **15**, 73; E. A. Blench and W. E. Garner, *J. Chem. Soc.*, 1924, **125**, 1288; H. v. Wartenberg and B. Sieg, *Ber.*, 1920, **53**, 2192.

¹ Similarly, hydrogen or carbon monoxide is reversibly sorbed by oxides of zinc, chromium or copper at room temperatures, but irreversibly at higher temperatures at which they can only be recovered as water and carbon dioxide; see W. E. Garner and F. E. T. Kingman, *Nature*, 1930, **126**, 352. Likewise, Langmuir found that the sorption of carbon monoxide by platinum is reversible at liquid air temperatures but irreversible at room and higher temperatures (see Chapter III, page 43, and Chapter IX, page 278, footnote 1).

² P. G. Tait and J. Dewar, *Proc. Roy. Soc. Edin.*, 1875, **8**, 628. For the attainment of extreme vacua through the chilling of non-volatile porous metals, see Miss M. A. Schirmann, *Physik. Z.*, 1926, **27**, 748.

³ J. Dewar, *Proc. Roy. Inst. Gt. Brit.*, 1905, **18**, 184.

experiments of Miss Homfray ¹ in England, Titoff ² in Germany, and Richardson ³ in America have been made the basis of many calculations in connexion with the rival explanations of sorption. Figs.⁴ 1, 2 and 3 present their isotherms or graphs of the amounts of sorption for different pressures at a series of constant temperatures.

Not only is the sorption much greater at low temperatures, but the isotherms are also much more curved. In other words, in the expression, $x/m = kp^{1/n}$, both k and n diminish

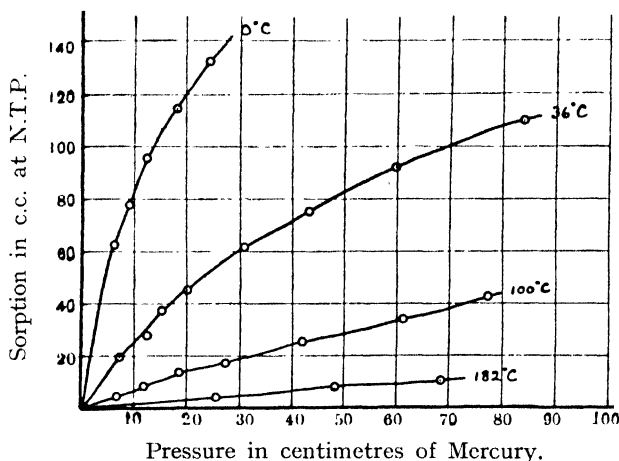


Fig. 1.—Sorption of Carbon Dioxide by Charcoal in c.c. at N.T.P. (Homfray).

continuously with rise of temperature, n in particular tending towards the value unity, so that sorption is more nearly proportional to the pressure.

However, in sorption from solutions, the effect of temperature is often different and may be in the opposite direction. Even with gases, especially where sorption is most nearly

¹ I. F. Homfray, *Z. physik. Chem.*, 1910, **74**, 129.

² A. Titoff, *Z. physik. Chem.*, 1910, **74**, 641.

³ L. B. Richardson, *J. Am. Chem. Soc.*, 1917, **39**, 1828.

⁴ J. W. McBain, *J. Soc. Dyers and Colourists*, 1923, **39**, 234.

identical with surface chemical reaction, sorption may persist to very high temperatures. For example, oxygen is firmly held on the surface of tungsten wires even at a white heat.

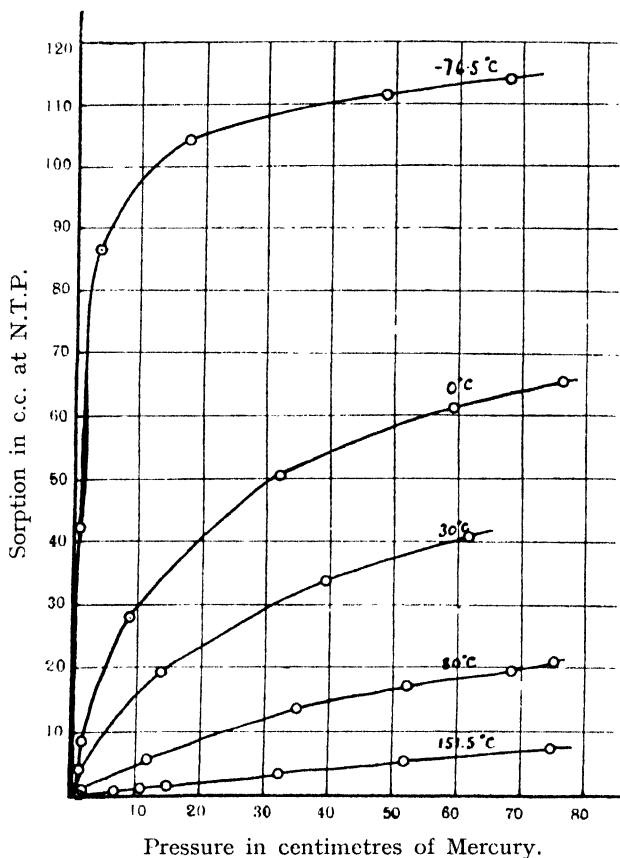


Fig. 2.—Sorption of Carbon Dioxide by Charcoal in c.c. at N.T.P. (Titoff).

SORBING AGENTS

It may help us to realize how universally sorption occurs if we consider a list of well-known sorbing agents whose sorbing actions have been studied. There comes first a whole

family of charcoals made from different materials under different conditions ; some of these are so porous and finely divided that a kilogram of the charcoal such as that used in defensive gas warfare is estimated to possess the equivalent of an effective surface of one million square metres. How extreme such a porosity must be is shown by the simple calculation that if that weight of carbon were rolled into one continuous sheet of graphite, the sheet would be 1.3 million square metres in area on each side. When 1 kilogram of active charcoal sorbs 500 c.c. of a liquid, which if spread out in a monomolecular layer would be 4 Å. thick and 1.25 million

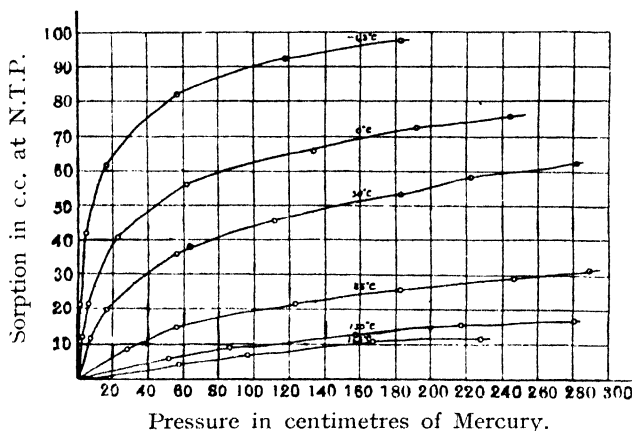


Fig. 3.—Sorption of Carbon Dioxide by Charcoal in c.c. at N.T.P. (Richardson).

square metres in extent, so thoroughgoing is the permeation of the structure by the sorbed material that the total area of contact between carbon atoms and sorbed molecules must be several million square metres.¹ This will be referred to

¹ O. Schmidt (*Z. physik. Chem.*, 1928, **133**, 263) calculates that the total surface of the water molecules removed on dehydrating chabasite, which retains its crystal structure, amounts to 3.8 million square metres per kilogram of chabasite. This equals or surpasses the ultra-porosity of the best active charcoal. Such chabasite can sorb as many as 1.4×10^{22} molecules of ammonia per cubic centimetre at room temperature and one atmosphere pressure (see Chapter V).

later in connexion with the author's term "persorption". In McBain and Britton's ¹ experiments the number of atoms of carbon in the activated sugar carbon is only nine times greater than the number of molecules of nitrogen it sorbs at -77°C . Other sorbing agents are meerschaum, wood, asbestos, mountain cork, wood, wool, cotton, silk, glass surfaces, glass wool, metal surfaces, platinum black, platinum sponge, mica, permutite, zeolites, fibrous alumina, pumice, silica gel, precipitates of hydroxide, china clay, fullers' earth, soil, filter paper, starch, lecithin, bile acids, proteins and cell colloids, etc. etc.² (See the Substance Index.)

SORPTION FROM SOLUTIONS

Sorption from solutions is frequently much more complex than sorption of gases or vapours, but the formula $x/m = kc^{1/n}$ often holds over an enormous range of concentrations. Frequently sorption is specific and is accompanied by chemical decomposition and interactions. Thus the substance deposited on a fibre has not necessarily either the composition or the properties of the dye in the original solution; many of these products are insoluble in water.

The separation of the constituents of a solution in this fashion is beautifully demonstrated by experiments with filter paper, in which the solution is allowed to rise by capillarity up a strip of filter paper or a drop is allowed to spread on the paper. Substances which are highly sorbed travel for a very short distance only, whereas those whose sorption is negligible reach the extreme edge of the wet zone. Probably the most important illustration of this selective action is the sorption of potassium compounds by soil.

The chemical aspects of sorption from solutions are often so prominent, even where the sorption formula is closely

¹ J. W. McBain and G. T. Britton, *J. Am. Chem. Soc.*, 1930, **52**, 2198.

² D. Lo Monaco, *Arch. farmacol. sper.*, 1920, **29**, 3; common materials, such as straw, hay, grass, soil, snow, fresh leaves, marine algæ, sawdust, charcoal and cotton, are capable, especially if moist, of sorbing to some extent the asphyxiating gases used in warfare.

followed, that many writers resent the emphasis that has been placed upon surface tension and thermodynamics in the theoretical discussion of the subject. However, enough has been indicated to show that these surface interactions obey distinctive laws, whatever their mechanism; and to the objections that these physical theories take too little account of specific chemical interaction, it is retorted that it is difficult to conceive of the practically instantaneous sorption of argon by charcoal at the temperature of liquid air as being a chemical process. The various cases of sorption are often in accordance with sweeping generalizations which cut across or submerge ordinary chemical experience. On the other hand, its occurrence is often decidedly specific; an example of this which is so extreme as to be embarrassing to a chemical interpretation is the observation of Nellensteyn¹ that diamond sorbs methylene blue but not succinic acid, whereas graphite sorbs succinic acid but not methylene blue. Such a conception as Langmuir's monomolecular adsorbed layer is an attempt to harmonize the various points of view, and it must be the chief object of this enquiry to examine the evidence as to the truth of the suggestion that only such molecules are sorbed as are actually in direct contact with the molecules of the adsorbing surface.

PRACTICAL IMPORTANCE

Space is lacking to enumerate the many practical applications of a knowledge of sorption. It occurs in every weighing, and to it is due the hygroscopic properties of precipitates, porous bodies and other materials. It must be avoided if really high vacua are to be obtained. It is prominent in the study of electric lamps and wireless valves. The properties of the soil are largely due to this action of the colloids therein. Formation of soil from the original rocks is partly due to its action. Spontaneous combustion of many substances in powdered form or with relatively large exposed surfaces is due to its occurrence. The analytical chemist takes special precautions during filtration and washing out of precipitates,

¹ F. J. Nellensteyn, *Chem. Weekblad*, 1925, **22**, 291.

and many great industrial operations are based upon it, such as decolorizing, deodorizing, tanning and dyeing, catalysis, flotation and lubrication. It is evident that there is a great need for an exact formulation and a clear-cut explanation of the phenomena and principles involved.

CHAPTER II

METHODS OF MEASUREMENT AND EVALUATION OF THE RESULTS

STANDARD METHOD

The crude method of Fontana was used for the greater part of the nineteenth century, but it is now long superseded by more carefully controlled procedures, which, however, still leave something to be desired. Nearly all the modern work has been carried out by enclosing a known weight of sorbing material in a bulb connected to a suitable manometer and surrounded by a thermostat. The contents of the bulb must previously be heated to remove gases and vapours and other impurities which are carried off by evacuation with a good pump.¹ The experiment consists in introducing a known amount of gas or vapour and in deducing the amount of sorption from a comparison of the observed pressure with that which would be expected if no sorption had occurred.

The fundamental difficulty lies in determining the "dead space" within the apparatus not occupied by the sorbing material itself. It is not serious if most of the substance introduced is sorbed and only a small fraction remains as vapour or gas in the dead space; but it may make the attempt at measurement worthless as soon as only a small fraction of an added sample is sorbed and the dead space is not known with sufficient accuracy. For this reason very few experimenters have attempted to study sorption at pressures above atmospheric or where the sorption, x/m , is changing but little with the pressure p .

Some of the methods employed to estimate the volume of

¹ Technique introduced by H. Kayser (*Wied. Ann. der Physik*, 1881, **12**, 526).

the dead space have been: (a) altering the pressure at a temperature much higher than that of the sorption experiment by introducing different amounts of gas, ignoring any sorption and assuming the gas laws; (b) by introducing a known amount of helium as an indifferent gas whose sorption is likely to be negligible and measuring the pressure produced;

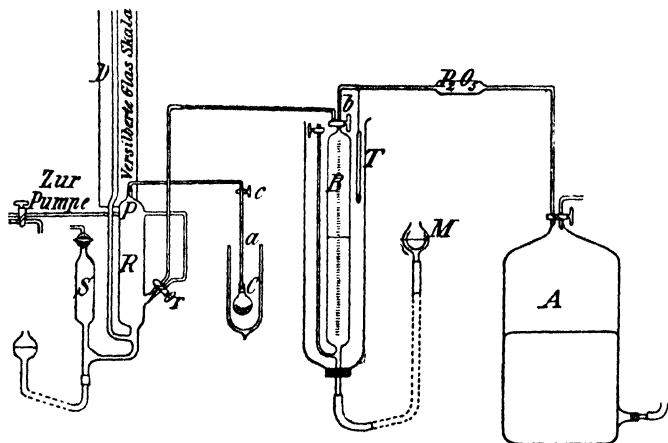


Fig. 4.—Sorption Apparatus of Miss Homfray.

(c) by measuring the interior of the glass apparatus and assuming a value for the density, and hence volume, of the sorbing material. (In the case of charcoal, as will be shown later, the true density has been a matter of much dispute.)

Some forms of sorption apparatus used by various investigators are illustrated by fig. 4 (Miss Homfray¹), fig. 5 (Titoff²), fig. 6 (Richardson³), fig. 7 (Coolidge⁴), fig. 8 (Zeise⁵) and fig. 9 (Goldmann and Polányi⁶). The latter used the device of removing sorbed vapour by successively cooling in

¹ I. F. Homfray, *Z. physik. Chem.*, 1910, **74**, 150.

² A. Titoff, *Z. physik. Chem.*, 1910, **74**, 642.

³ L. B. Richardson, *J. Am. Chem. Soc.*, 1917, **39**, 1829.

⁴ A. S. Coolidge, *J. Am. Chem. Soc.*, 1924, **46**, 603.

⁵ H. Zeise, *Z. physik. Chem.*, 1928, **136**, 388, fig. 1.

⁶ F. Goldmann and M. Polányi, *Z. physik. Chem.*, 1928, **132**, 329.

liquid air a series of forty side tubes attached to the apparatus, each of which was sealed off and weighed. However, this cannot have obviated the quite appreciable error which is due to the dead space as previously pointed out.

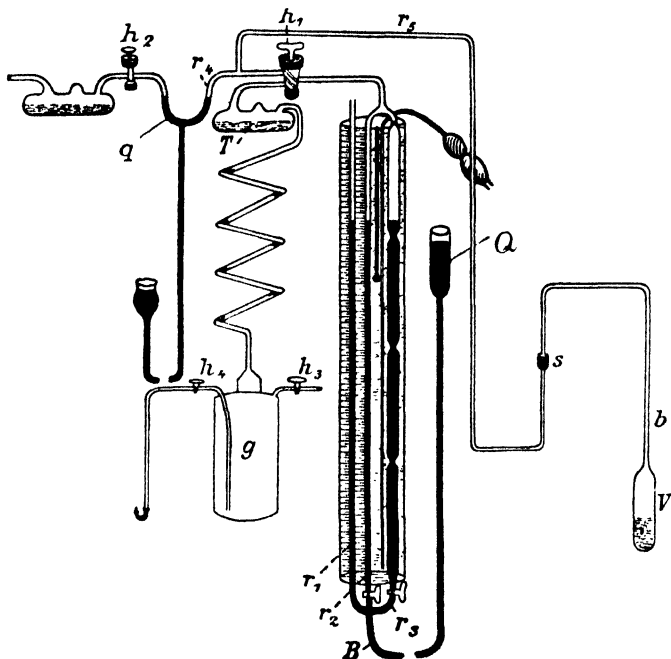


Fig. 5.—Sorption Apparatus of Titoff.

SORPTION BALANCES

The use of a sorption balance such as that of McBain and Bakr,¹ fig. 10, or McBain and Tanner,² which can be enclosed within an entirely sealed-up system which need not be opened throughout the whole series of measurements, possesses many

¹ J. W. McBain and A. M. Bakr, *J. Am. Chem. Soc.*, 1926, **48**, 693; P. T. Newsome, *Ind. Eng. Chem.*, 1928, **20**, 827; see Chapter XII, page 363, fig. 112.

² J. W. McBain and H. G. Tanner, *Proc. Roy. Soc. (London)*, A, 1929, **125**, 579.

essential advantages in addition to eliminating any significance attaching to the dead space.

The McBain-Bakr balance, now extensively used, consists

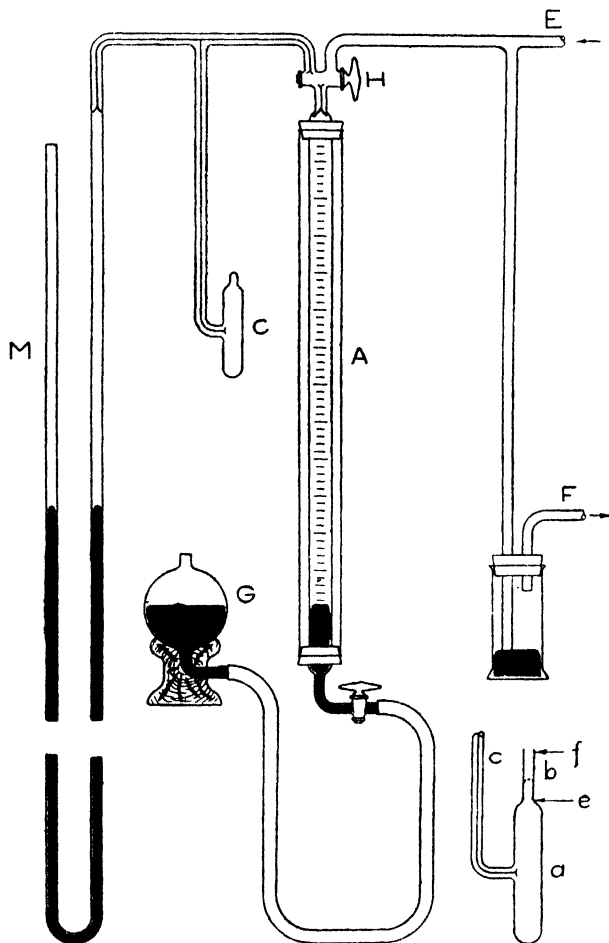


Fig. 6.—Sorption Apparatus of Richardson.

of a helical spring of fused silica whose extension measures the weight of sorbing material in a bucket hanging from it as well as weighing directly any material which is subsequently

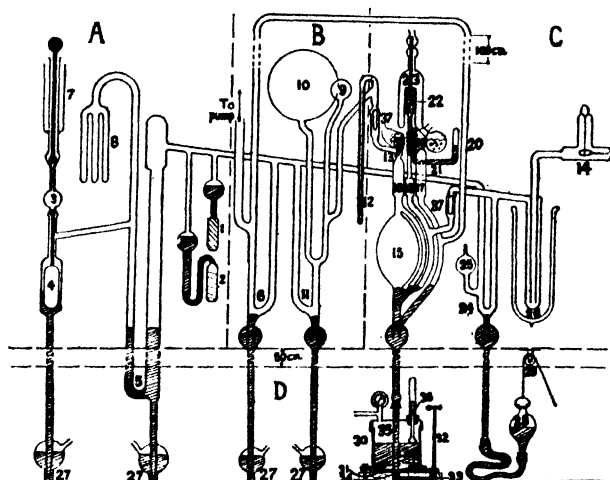


Fig. 7.—Sorption Apparatus of Coolidge.

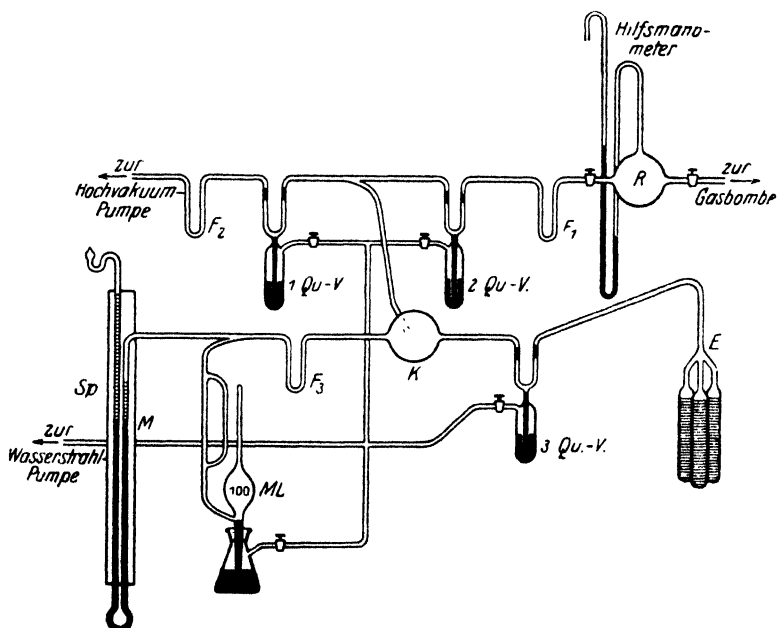


Fig. 8.—Sorption Apparatus of Zeise.

sorbed. Sorption and desorption can be observed directly and repeatedly under a whole series of experimental conditions without the fear that through accidental treatment the activity of the sorbing material might be altered. Pressure within the apparatus may be very conveniently adjusted in the case of vapours by cooling a portion of the glass tubing to various temperatures and having sufficient vapour present to keep some liquid condensed, whereupon its vapour pressure will be the pressure prevailing throughout the apparatus. Dühring's rule¹ is a convenient and accurate method of evaluating the

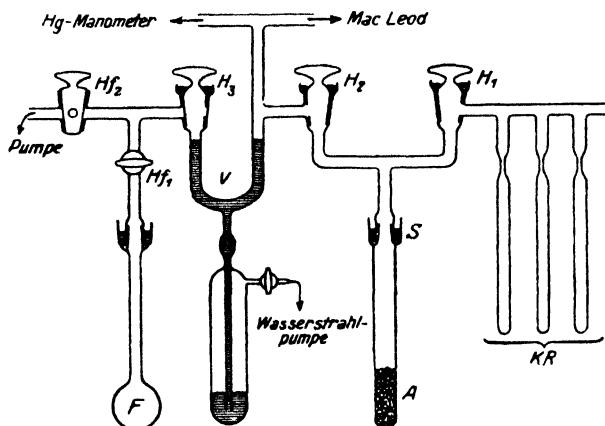


Fig. 9.—Sorption Apparatus of Goldmann and Polányi.

vapour pressures for this purpose. The range of pressure may be anything that the apparatus can withstand. The silica spring should be annealed by heating under load to a temperature higher than any at which it will subsequently be used.² Buoyancy correction is not serious except at very

¹ U. Dühring, *Neue Grundgesetze zur Rationelle Physik und Chemie*, Leipzig, 1878; R. Lorenz, *Z. anorg. allgem. Chem.*, 1924, **138**, 104; E. H. Leslie and A. R. Carr, *Ind. Eng. Chem.*, 1925, **17**, 810; A. R. Carr and D. W. Murphy, *J. Am. Chem. Soc.*, 1929, **51**, 116; A. McLaren White, *Ind. Eng. Chem.*, 1930, **22**, 230. Compare F. C. Kracck, *J. Phys. Chem.*, 1930, **34**, 499.

² H. D. H. Drane, *Proc. Roy. Soc. (London)*, A, 1929, **122**, 274; A. A. Griffith, *Phil. Trans. Roy. Soc. (London)*, 1920, **221**, 163.

high pressures and may be allowed for by calculation from the density of the vapour.

The McBain-Tanner balance is a robust microbalance of extreme sensitivity (10^{-9} gm.) which may be placed in a glass tube. It possesses the great advantage of being of the beam type with nearly equal volumes on both sides of the balance so that buoyancy effects are almost eliminated. By using an alternating current solenoid operating upon a piece of soft iron sealed within the fused silica, it is used with the null method of restoring the balance to its original position by passing the appropriate current through the solenoid.

Other experimenters who have used different balances in the study of sorption are Ihmori,¹ Giesen,² Aharoni,³ Wulff⁴ and Strömberg.⁵

Seeliger's⁶ torsion balance again introduces the error of the dead space within the sorbing material and its container. Harned⁷ connected the bulb containing the sorbing material through a tap and ground joint to the remainder of the apparatus so that it could be removed and weighed (including the vapour in the dead space). Weigel and Steinhoff⁸ describe an arrangement for opening and closing a weighing vessel within the sorption apparatus.

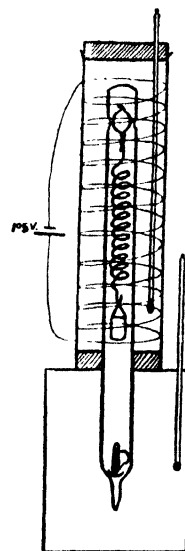


Fig. 10.—McBain-Bakr Sorption Balance.

¹ E. Warburg and T. Ihmori, *Wied. Ann. der Physik*, 1886, **27**, 481; T. Ihmori, *Wied. Ann. der Physik*, 1887, **31**, 1006.

² J. Giesen, *Ann. der Physik*, (4), 1903, **10**, 838, who used a Salvioni microbalance sensitive to 10^{-6} g.

³ J. Aharoni, *Dissert.*, Berlin (1929).

⁴ J. Wulff, *Nature*, 1929, **123**, 682.

⁵ R. Strömberg (*Kgl. Svenska Vetenskapsakad. Handl.*, (3), 1928, **6**, No. 2, 1) who developed and used a beam microbalance sensitive to 3×10^{-9} g.

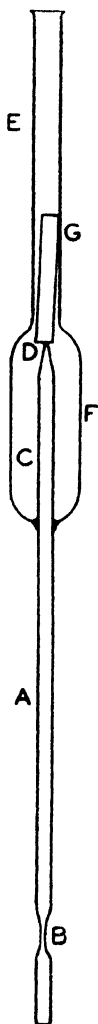
⁶ R. Seeliger, *Z. Physik.*, 1921, **4**, 189.

⁷ H. S. Harned, *J. Am. Chem. Soc.*, 1920, **42**, 372.

⁸ O. Weigel and E. Steinhoff, *Z. Krist.*, 1925, **61**, 125.

SORPTION OF MIXTURES

Bakr and King's ¹ method of studying the sorption of mixed vapours, although laborious, is still the best for this purpose. It consists of two bulbs connected by a tube. One bulb contains the mixed liquids and is maintained at a lower temperature than the other which contains the sorbing material, the total pressure being regulated by adjusting the temperature of the cooler bulb. When equilibrium is reached, the tube is sealed, and the two halves of the apparatus are weighed separately with appropriate corrections, the liquid being analysed. The disadvantage is that each experiment yields only one isolated value for sorption.



SORPTION PIPETTE

Jenkins and Bennett ² have developed the simplest method of studying sorption of vapours under all conditions where errors due to the dead space are not too serious. Their apparatus, the "sorption pipette", fig. 11, "consists essentially of a pipette, the bottom portion of which is a tube *A* graduated in 1/20 c.c. and constricted at *B*. An ungraduated extension *C* is sealed off at *D* where the top portion *E* of the pipette joins the middle part *F*". The tube *A* is filled with air-free liquid and sealed off at *B* during evacuation.

¹ A. M. Bakr and J. E. King, *J. Chem. Soc.*, 1921, **119**, 454.

Fig. 11.—Sorption Pipette of Jenkins and Bennett.

² W. J. Jenkins and H. B. Bennett, *J. Phys. Chem.*, 1930, **34**, 2318; used by H. H. Lowry, *J. Phys. Chem.*, 1930, **34**, 63. An essentially similar apparatus is described by F. A. Henglein and M. Grzenkowski (*Z. angew. Chem.*, 1925, **38**, 1186) and by M. Guichard (*Bull. soc. chim.*, (4), 1922, **31**, 552).

After introducing the porous sorbing material and the loose glass rod *via E*, the pipette is evacuated and sealed off at *F*. The sorption can now be studied under any desired series of conditions without again opening the tubing, the amount of sorption being deduced from the change in height of the liquid meniscus in the graduated tube *A*. This apparatus contains no delicate parts and requires no expert manipulation, and its use may be recommended for introductory courses in physical chemistry. Heating coils may be improvised from nichrome wire laid upon asbestos stiffened with sodium silicate. The only necessary precaution during the measurement is that no part of the tube or upper cylinder is at a lower temperature than the liquid below.

DYNAMIC METHODS

Particularly for practical purposes, such as the testing of masks used in gas warfare, dynamic methods are employed.¹ For example, the vapour or gas to be sorbed is drawn in a current of indifferent gas over the sorbing material for a given length of time or until the composition of the issuing gas is that of the original. A reversal of this method is that of Allmand, Manning and Burrage. A known weight of charcoal is saturated with the vapour, reweighed, and through it is passed dry air, the charcoal being weighed at intervals. Another special method of studying both amount and heat of sorption, with certain assumptions, is that of Palmer² who uses a coherer.

¹ A. B. Lamb, R. E. Wilson and N. K. Chaney, *J. Ind. Eng. Chem.*, 1919, **11**, 420; A. C. Fieldner, G. G. Oberfell, M. C. Teague and J. N. Lawrence, *J. Ind. Eng. Chem.*, 1919, **11**, 519; G. S. Bohart and E. Q. Adams, *J. Am. Chem. Soc.*, 1920, **42**, 523; E. V. Alekseevski, *J. Russ. Phys. Chem. Soc.*, 1924, **55**, 401; A. J. Allmand and J. E. Manning, *J. Soc. Chem. Ind.*, 1928, **47**, 369T; A. J. Allmand and L. J. Burrage, *J. Soc. Chem. Ind.*, 1928, **47**, 372T; L. J. Burrage, *J. Phys. Chem.*, 1930, **34**, 2202; R. Lorenz and E. Wiedbrauck, *Z. anorg. allgem. Chem.*, 1924, **134**, 251, with a few results for mixtures of hydrogen, oxygen, nitrogen and carbon dioxide by charcoal; N. A. Shilov, L. K. Lepin and S. A. Voznesenskii, *Kolloid-Z.*, 1929, **49**, 288; *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 1107; chlorine by charcoals.

² W. G. Palmer, *Proc. Roy. Soc. (London)*, A, 1924, **106**, 55; 1926, **110**, 133. See also R. H. Wright and M. J. Marshall, *Trans. Amer. Electrochem. Soc.*, 1928, **54**, 149.

THE OPTICAL METHOD

The optical method of studying sorption on truly smooth surfaces has not been fully enough exploited and its results have often been accepted with reserve. This is partly due to the fact that investigations of surfaces demand all the precautions of the best chemical work but in a superlative degree. The real difficulty is to obtain a surface clean enough to be worth using in the study of sorption.

The method¹ uses plane polarized light, whose plane of polarization is at an angle of 45 degrees to a smooth surface and which is reflected from that surface. In general, the two components, parallel to and perpendicular to the plane of incidence, are changed in amplitude and in phase, the reflected light becoming elliptically polarized as may be tested by examination with a Babinet compensator. The two components differ in phase as well as amplitude. The change in phase is readily measured. Reeser and Sissingh² have developed a method for also measuring the "restored azimuth" Ψ when $\tan \Psi$ is the ratio of the two amplitudes. The values depend upon the angle of incidence. The angle of incidence, for which the difference in phase is equal to $\pi/2$, is called the angle of principal incidence I and the corresponding value of Ψ is called the principal azimuth H .

According to Lorenz³ ellipticity is due to any departure from a mathematically sharp plane surface of separation between the two homogeneous phases, gas and solid. This can be caused by roughnesses or vibrations or, more important from our standpoint, by any sorbed layer or zone of intermediate refractive index. Formulæ and methods for the quantitative evaluation of the transition or sorption layer have been developed by Drude⁴ and others.

¹ See especially the lucid account given by J. Ellerbroek, *Arch. Néerland Sci.*, Series IIIA, 1927, **10**, 42.

² C. A. Reeser and R. Sissingh, *Proc. Acad. Sci. Amsterdam*, 1922, **24**, 108.

³ L. Lorenz, *Pogg. Ann. der Physik*, 1860, **111**, 460; 1861, **114**, 238.

⁴ P. Drude, *Wied. Ann. der Physik*, 1890, **39**, 481; 1889, **36**, 536, 865. See also Chapter VIII, page 253, footnote 2.

For examples of the use of the method see Chapters VII, pages 231 and 232; VIII, page 253; and IX, page 270. The measurement of ellipticity gives in effect the amount of material in the sorption layer. The determination of the restored azimuth gives directly the refractive index of the sorbed layer which may yield valuable information as to its chemical nature.

SORPTION OF SOLUTIONS

Sorption from solutions is always studied by immersing a known amount of sorbing material in a known amount of solution and determining the change in concentration of the solution when equilibrium has been reached. The amounts taken are usually adjusted so that the original and final concentrations are both capable of accurate analysis. The experiments become inexact for very large or very small amounts of sorbing material. Measurements taking into account the sorption of solvent as well as solute require the combination of this kind of experiment with that of a study of the sorption of the vapour. Adsorption in a surface of a pure liquid or a solution lies outside the scope of the present volume.

PRECAUTIONS

In all the static methods certain precautions have to be taken. The one that can hardly be sufficiently stressed is the necessity for drastic evacuation of the apparatus and especially the sorbing material at as high a temperature as possible and for a prolonged period. For example, in the case of charcoal, evacuation for two days at 600° and a pressure not exceeding 10^{-4} mm. may not only double the amount of sorption but may entirely alter the form of the curve connecting sorption with pressure. All extraneous gases and impurities should be removed. Sources of such admixtures are glass stop cocks, lubricants used with them, and mercury vapour, as, for example, when mercury is substituted for glass stop cocks, or when no mercury trap employing gold or liquid air is interposed between all mercury surfaces and the sorbing material. The weight of mercury which

can be sorbed by one gram of carbon under favourable conditions amounts to over 6 per cent.¹ Pressure within the apparatus is often read by means of a mercury manometer or a McLeod gauge or, for low pressures, by observing the logarithmic decrement of the vibrations of a single or double filament of fused silica. Other devices include use of a katharometer,² ionization gauge, etc. Young³ has described a simple and extremely delicate method for testing liquids for any gases dissolved therein.

It is always necessary to test whether equilibrium has been established. The most effective method is to approach it by both sorption and desorption allowing sufficient time for the two results to coincide.

In the usual mode of experiment, sorption by the glass walls of the apparatus cannot always be ignored and has to be allowed for by blank experiment. Care has likewise to be taken to avoid unnecessary capillary spaces in the sorbing material in which nearly saturated vapours might condense.

CALCULATION

The results, by whatever method obtained, are usually tested for conformity with the empirical formula, $x/m = kp^{1/n}$ or $kc^{1/n}$. The simplest and most effective way of doing this is to plot the logarithm of x/m against the logarithm of p or c , because this equation in the form $\log \frac{x}{m} = \log k + \frac{1}{n} \log p$ yields a straight line if it is applicable to the data. The purely empirical constants k and n are evaluated by noting the slope of the line, which is $1/n$, and its intercept with the $\log x/m$ axis for $\log p = 0$ (or $p = 1$), which is $\log k$.

¹ A. S. Coolidge, *J. Am. Chem. Soc.*, 1927, **49**, 708, 1949; N. D. Zelinsky and M. A. Rakusin, *Ber.*, 1926, **59B**, 2072; and indications by older workers.

² H. A. Daynes and G. A. Shakespear, *Proc. Roy. Soc. (London)*, A, 1920, **97**, 273; G. A. Shakespear, *Proc. Phys. Soc. (London)*, 1921, **33**, 163; F. Simon, *Z. physik. Chem.*, 1928, **132**, 456.

³ F. B. Young, *Phil. Mag.*, (6), 1910, **20**, 793; cf. F. G. Keyes and W. A. Felsing, *J. Am. Chem. Soc.*, 1919, **41**, 604.

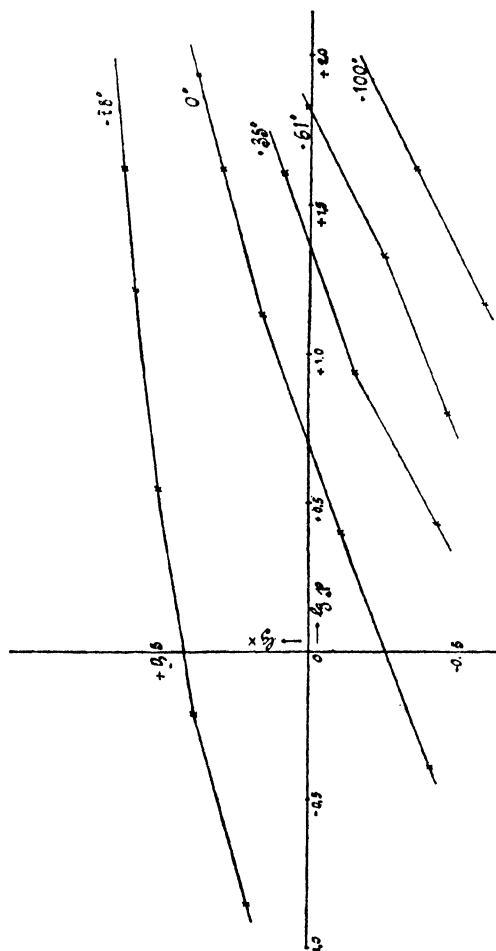


Fig. 12.—Sorption of Carbon Dioxide by Charcoal. Data of Travers graphed according to the exponential formula. The abscissae are the logarithms of the pressure (in centimetres of mercury) and the ordinates are the logarithms of the weight of Carbonic Acid sorbed by 100 grams of Charcoal.

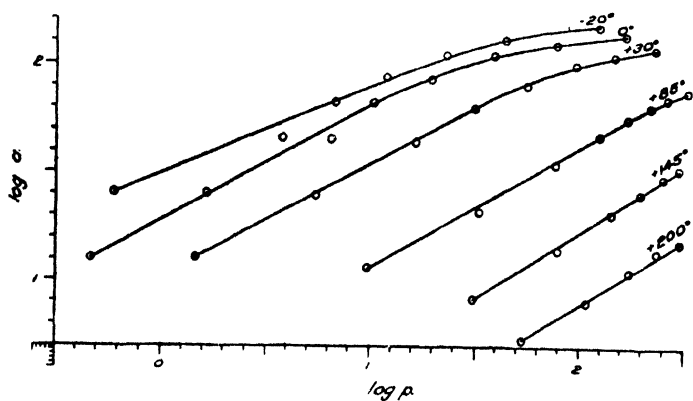


Fig. 13.—Sorption of Ammonia by Charcoal. Richardson's data graphed according to the exponential formula (a = volume of gas sorbed by 1 gram of Charcoal).

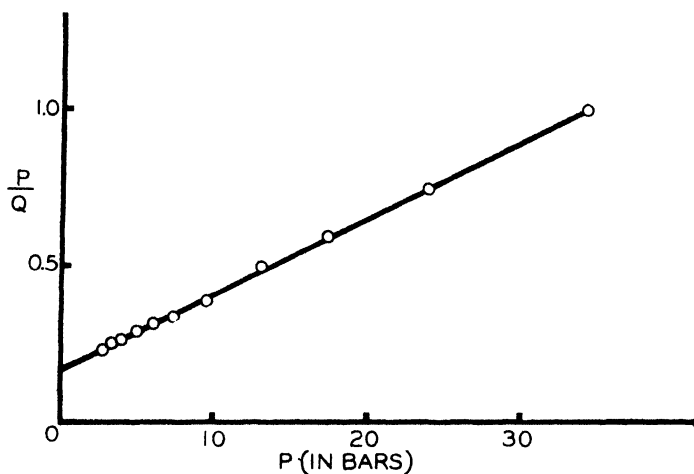


Fig. 14.—Data for the Sorption of Nitrogen by 24.3 g. of mica (area 5.750 sq. cm.) at 90° K. graphed according to the Langmuir equation (Q = amount of Gas sorbed expressed in cu. mm. at 20° and 760 mm. pressure).

Similarly, the Langmuir formula,¹ $\frac{x}{m} = \frac{abp}{1 + ap}$, where a and b are constants, may be tested and the constants evaluated by plotting in the form of the linear equation, $\frac{p}{x/m} = \frac{1}{ab} + \frac{p}{b}$,

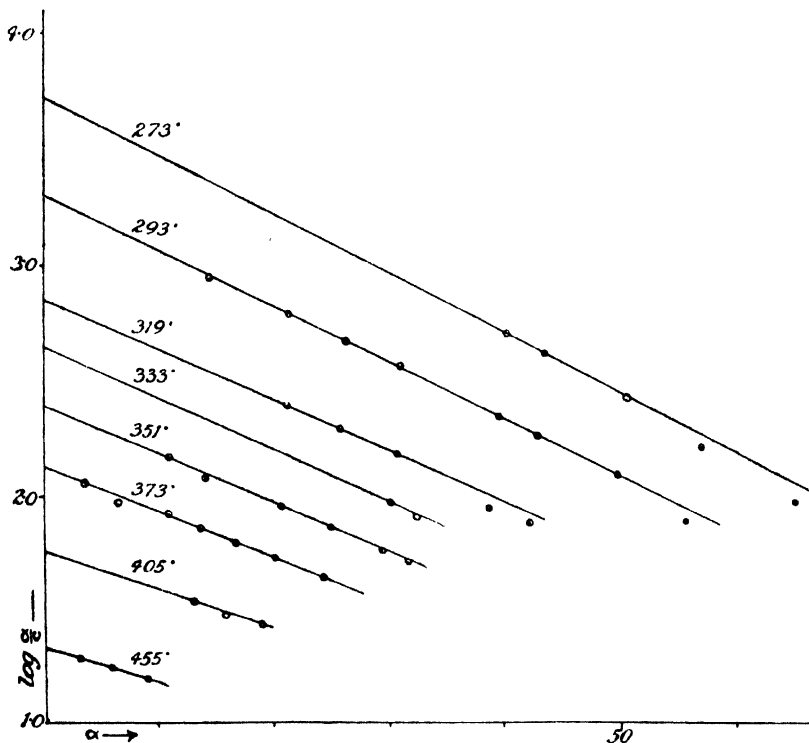


Fig. 15.—Sorption of Ethylene by Coconut Charcoal. Data of Miss Homfray graphed by Williams according to the Williams formula ($a = x/m$ and $c = p/RT$).

where in the graph of $\frac{p}{x/m}$ against p , $1/b$ is the slope of the straight line and $1/ab$ is the intercept or ordinate for $p = 0$. Typical data evaluated according to these two formulæ, which

¹ I. Langmuir, *J. Am. Chem. Soc.*, 1918, **40**, 1384.

are mutually incompatible, are shown in figs. 12,¹ 13,² and 14.³ For very low pressures, according to Langmuir's equation, the value of n must approach unity.

The most exacting equation by which to test experimental results is the Williams-Henry formula,⁴ $\log \frac{x/m}{p} = k_1 - k_2 \frac{x}{m}$, which likewise reduces to Henry's law ($n = 1$) for infinitesimal pressure. Sorption data which obey this formula, derived independently both from general kinetic considerations and also from a particular form of the Langmuir conceptions, give straight lines as in fig. 15.⁵

¹ H. Freundlich, *Z. physik. Chem.*, 1907, **61**, 250.

² L. B. Richardson, *J. Am. Chem. Soc.*, 1917, **39**, 1843.

³ Data of I. Langmuir, *J. Am. Chem. Soc.*, 1918, **40**, 1383.

⁴ A. M. Williams, *Proc. Roy. Soc. (London)*, A, 1919, **96**, 287, 298; D. C. Henry, *Phil. Mag.*, (6), 1922, **44**, 689; E. Jaquet, *Fortschritte Chem., Physik, physik. Chem.*, 1925, **18**, Heft 7, 1.

⁵ A. M. Williams, *Proc. Roy. Soc. (London)*, A, 1919, **96**, 299, fig. 4.

PART II

THE EXPERIMENTAL DATA

CHAPTER III

GENERAL BEHAVIOUR

It is advisable to review the empirical facts before attempting theoretical explanations. Attention will be directed chiefly to gases and vapours because these represent the simplest cases and are most likely to lead to general theories.

SIGNIFICANCE OF THE FORMULÆ DESCRIBING SORPTION

The empirical formula, $x/m = kp^{1/n}$, applies fairly well over medium ranges for gases and vapours, as is illustrated in Chapters I and II for the sorption of carbon dioxide by charcoal, figs. 1, 2, 3, 12; of ammonia by charcoal, fig. 13; of hydrogen by animal charcoal, fig. 16.¹ The shape of these curves for the change of sorption with pressure may be contrasted with that required for Henry's law, or a distribution ratio between two homogeneous phases which demand a direct proportionality between x/m and p as shown by the straight line in fig. 17. Again, a distribution ratio in which association occurred in the solid phase would be represented by a curve which is concave upwards as in fig. 18. Finally, the phase rule for equilibria between a gas and solid phases of definite composition would require the still different type of graph shown in fig. 19, where none of the gas combines below a definite pressure, and the pressure thereupon remains constant until the reaction is completed.

The fact that the sorption curve is continuous down to the

¹ A. Titoff, *Z. physik. Chem.*, 1910, **74**, 651.

lowest pressures is of great practical significance. This is forcibly illustrated by considering the effect of diminished pressure upon the sorption of vapour for which $n = 5$; that is, the sorption varies as the fifth root of the pressure. To halve any given value of sorption, the pressure would have to

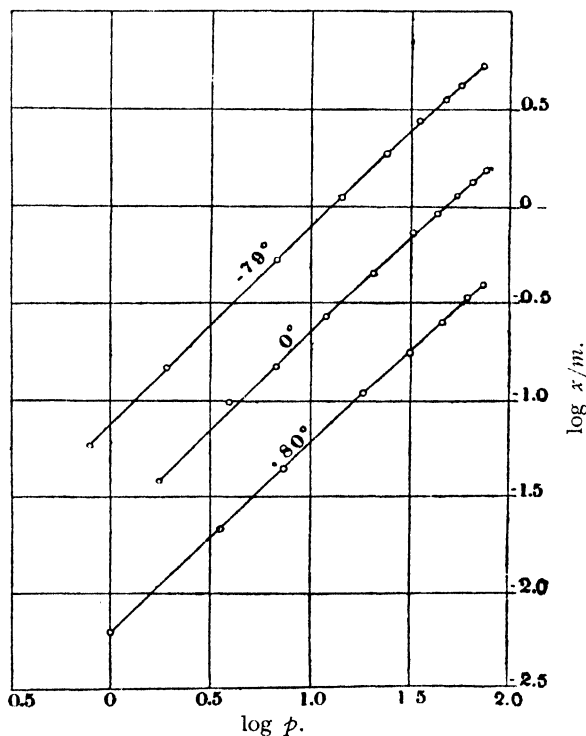


Fig. 16.—Sorption of Hydrogen by Animal Charcoal, graphed according to the Exponential Formula (Titoff).

be diminished 32-fold. To reduce a given value of x/m to 0.1 per cent of its previous value, the pressure would have to be diminished in the proportion of 10^{15} -fold, an operation which cannot be accomplished experimentally. Hence the elimination of sorption by mere evacuation is never complete. For example, in the sorption of toluene by a fairly clean

surface of charcoal, reduction of the pressure from one atmosphere to $1/20,000$ of this value leaves the sorption of the toluene still about one-half of its original value (see Chapter IV, pages 128 and 130, figs. 44 and 46).

The same conclusion from the continuous nature of the sorption equilibrium curve is reached by considering the free energy of sorption which is $RT \ln 1/p$ for a gas and RT

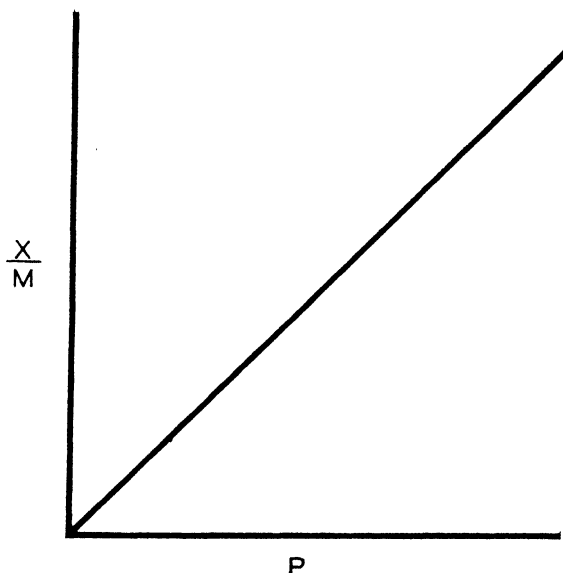


Fig. 17.—Distribution Ratio of a Substance between two Homogeneous Phases in which it has the same Molecular Weight.

$\ln p_s/p$ for the vapour of a liquid whose vapour tension is p_s . In both cases the free energy or tendency for sorption to take place, that is, for one gram mol to be sorbed by an infinitely large amount of solid, becomes infinitely great as the pressure p becomes zero. It is for this reason that traces of sorption become prominent as soon as surfaces become highly developed. This universal behaviour of sorption is superimposed upon ordinary chemical equilibria so that in practice diagrams such as fig. 19 are sometimes considerably

distorted or altered from the strict requirements of the phase rule; the perpendicular line ceases to be quite vertical and the top and bottom corners are rounded.

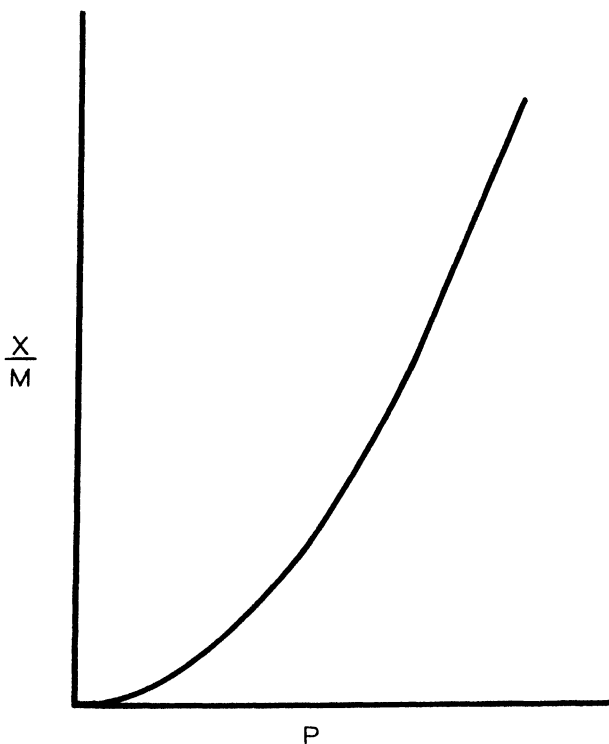


Fig. 18.—Distribution Ratio to be anticipated if there is association of the Dissolved Substance in Homogeneous Solid Phase.

SORPTION AT LOW PRESSURES

The above considerations are not invalidated by the fact that all the theories of sorption agree in postulating that for sufficiently low pressures the value of n becomes equal to unity. This is equally true in the Langmuir formulation, $\frac{x}{m} = \frac{abp}{1 + ap}$, and in the potential or compressed film theories,

where for infinitesimal pressure the sorption equation becomes a distribution of a perfect, highly dilute gas between the sorption region in the neighbourhood of the solid and the surrounding atmosphere. These conditions are difficult to realize in practice except for permanent gases or at high temperatures.

Dewar ¹ obtained the values given in table 2 for the sorp-

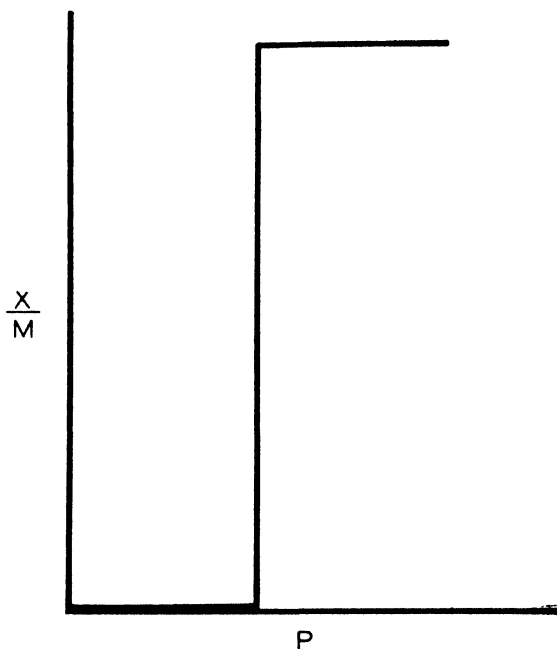


Fig. 19.—Equilibria between a Gas and Solid Phases where the latter are of definite composition, as for example, the Vapour Pressures of a series of definite Hydrates or the pressure of Carbon Dioxide above Calcium Oxide and Calcium Carbonate.

tion of hydrogen and nitrogen by 25 gm. of charcoal at the temperature of liquid air; pressures were read on a McLeod gauge. It is seen that for sufficiently low pressures the sorption becomes directly proportional to the pressure, but

¹ J. Dewar, *Proc. Roy. Inst. Gt. Britain*, 1907, **18**, 751.

only for very low pressures. The data likewise illustrate the great difference in amount of sorption at a given pressure and temperature between hydrogen and nitrogen.

TABLE 2

Dewar's Values for the Pressures Corresponding to Different Amounts of Sorption of Hydrogen and Nitrogen by 25 gm. of Charcoal at the Temperature of Liquid Air

Volume of gas sorbed c.c.		Occlusion hydrogen pressure mm.	Occlusion nitrogen pressure mm.
0		0.00003	0.00005
5		0.0228	—
10		0.0455	—
15		0.0645	—
20		0.0861	—
25		0.1105	—
30		0.1339	0.00031
35		0.1623	—
40		0.1870	—
130		—	0.00110
500		—	0.00314
1,000		—	0.01756
1,500		—	0.02920
2,500		—	0.06172

Rowe¹ studied the sorption of carbon monoxide, nitrogen and hydrogen by charcoal at -183°C . and observed that at extremely low pressures, within the experimental error, the sorption was proportional to the pressure. This is illustrated by fig. 20.² Similar results were obtained with nitrogen, carbon monoxide, oxygen and carbon dioxide at room temperatures and very low pressures.³

Similarly, Chaplin⁴ determined the isotherm for nitrogen on charcoal at 25° between 2×10^{-4} and 1.3×10^{-2} mm. of mercury. At this temperature and pressure the quantity of

¹ H. Rowe, *Phil. Mag.*, (7), 1926, **1**, 1042.

² H. Rowe, *Phil. Mag.*, (7), 1926, **1**, 1048, fig. 2.

³ H. Rowe, *Phil. Mag.*, (7), 1926, **1**, 109. On the other hand, A. Clemente (*Dissert.*, Chicago, 1924) found that with activated coconut charcoal and benzene at room temperature Henry's law did not hold at pressures above about 10^{-5} cm., below which the data were irregular.

⁴ R. Chaplin, *Phil. Mag.*, (7), 1926, **2**, 1198.

nitrogen sorbed is a linear function of the pressure. Coolidge ¹ found that below a relative humidity of one-tenth of the saturation pressure of liquid water the sorption of water vapour by charcoal obeys Henry's law at 100° and 218° C. Other examples are quoted in Chapter IV.

Polányi and Welke ² in three single isotherms for sulphur dioxide on commercial activated charcoal at pressures between 5×10^{-5} to 1.6×10^{-3} , 1×10^{-4} to 6×10^{-3} and 7×10^{-4}

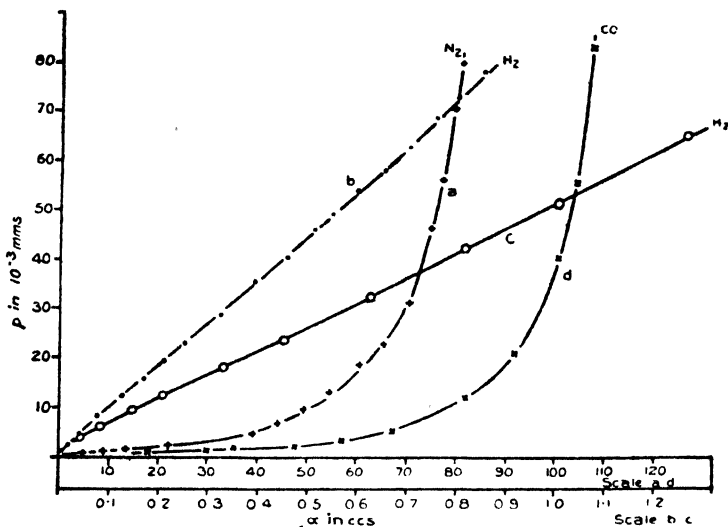


Fig. 20.—Rowe's Isotherms for the Sorption of Carbon Monoxide, Nitrogen and Hydrogen by Charcoal at -183° C. (α = volume of Gas at N.T.P. sorbed per gram of Charcoal).

to 2.8×10^{-1} mm. Hg obtain in each case curves with points of inflection which depart in opposite directions from Henry's law and do not conform with it even at the lowest pressures. Their data are thus at variance with all other experience in this field. Until their work is confirmed and the necessary blank experiments carried out, the elaborate

¹ A. S. Coolidge, *J. Am. Chem. Soc.*, 1927, **49**, 714.

² M. Polányi and K. Welke, *Z. physik. Chem.*, 1928, **132**, 371. See Chapter IV, page 117, footnote 3.

explanations which they set up for each part of this pressure range may be left for reference to the original.

Henry's law is followed by silica gel up to much higher pressures than with charcoal. Thus for carbon dioxide ¹ it holds at 0° C. up to 1 mm., and at other temperatures up to the same amount of sorption ($x/m = 0.00032$ gm. carbon dioxide per one gram of silica gel); hence at 100° C. sorption is a linear function of the pressure up to 400 mm. pressure.

Zeise ² in experiments with methane, nitrogen, oxygen and hydrogen on glass at -183° and at pressures between 0.0002 and 0.07 mm. found the sorption initially proportional to the square root of the pressure. Langmuir, ³ on the other hand, pointed out that for metallic surfaces upon which diatomic gases are separated into atoms, the amount of such sorption must depend, even at low pressures, upon the square root of the pressure. The same would also be true for absorption or solution as atoms.

Allmand and Burrage ⁴ have finally come to the conclusion that all isotherms for porous bodies such as charcoal and silica gel should consist of a series of discontinuous curves. Most investigators ascribe any such irregularities to experimental error and to fluctuations in experimental conditions, impurities, etc. More careful work in sealed systems is required to prove the reality of the suggested discontinuities.

ISOBARS AND ISOSTERES

Whereas isotherms represent amounts of sorption at various pressures or concentrations at a constant temperature, isobars portray the amounts of sorption at various temperatures for a given constant pressure, and isosteres show the pressures

¹ A. Magnus and R. Kieffer, *Z. anorg. allgem. Chem.*, 1929, **179**, 217. The results of W. Kälberer and C. Schuster are in conflict with these findings; they obtain deviations from linearity in both directions (*Z. physik. Chem.*, Abt. A, 1929, **141**, 278; see also H. Kälberer, H. Mark and C. Schuster, *Z. Elektrochem.*, 1929, **35**, 600).

² H. Zeise, *Z. physik. Chem.*, 1928, **136**, 385.

³ I. Langmuir, *J. Am. Chem. Soc.*, 1918, **40**, 1373.

⁴ A. J. Allmand and L. J. Burrage, *Proc. Roy. Soc. (London)*, A, 1931, **130**, 610.

required to produce the same amount of sorption at various temperatures. The more characteristic forms of isotherms have been mentioned in Chapter II. An idea of the general appearance of an isobar is given in Chapter IV, page 98, fig. 26, in which a somewhat curved line represents the diminution in the value of $\log p$ when plotted against temperature. A much more exact description of typical isosteres is given by the statement that the logarithm of the pressure diminishes linearly with the reciprocal of the absolute temperature. (See also the formulation of isosteres by Williams¹ and fig. 147 in Chapter XVIII, page 492.) Lannung² shows that the same method of plotting against the reciprocal of the absolute temperature gives straight line graphs for the logarithm of the solubility of the noble gases in organic solvents.

For more systematic discussion of the subject of isobars and isosteres reference should be made to H. Freundlich's *Kapillarchemie*, 1930, Bd. I, page 161, where it is pointed out that an isostere corresponds completely to the vapour pressure curve of a pure liquid or of a mixture of constant composition. The restriction which the writer places upon this dictum of Freundlich, resulting from the hypothesis of steric hindrance and strain, is discussed in Chapter IV, page 141 and 142.

STERIC HINDRANCE IN SORPTION

The writer would suggest that steric hindrance³ plays an essential part in sorption phenomena. In this he is not so much referring to the configuration of active portions of the molecule as to the simple primary truth that atoms and molecules occupy a space and that the irreducible minimum is but little less than that occupied by a corresponding amount of free liquid. Hence neighbouring molecules get in each

¹ A. M. Williams, *Proc. Roy. Soc. (London)*, A, 1919, **96**, 298.

² A. Lannung, *J. Am. Chem. Soc.*, 1930, **52**, 76.

³ I. Langmuir (*J. Am. Chem. Soc.*, 1917, **39**, 1902) introduced the term and conception of steric hindrance into this subject, but he did not predict the expansion of the solid which is necessitated by the present argument and which was sought at the writer's suggestion (see Chapter XIII).

other's way and prevent complete satisfaction of the valencies or attractive forces potentially present.

Even on plane surfaces sorption suffers from steric hindrance. An extreme illustration is afforded by the sorption of a dye on crystal surfaces as studied by Paneth and his collaborators,¹ where, for example, room is found for only one molecule of Ponceau Red 2R upon seventeen molecules of exposed lead sulphate each of which has an equal potentiality. Perfect sorption is an unattainable ideal which would be exhibited only if each molecule of the solid could be held at a distance from all the others by some tie which would not interfere with the exposure or strength of its valencies.

Sorption depends upon the nature of the exposed valencies, using this term in the broadest sense, primary and residual. Still more especially it depends upon the mechanical structure of the solid and the dimensions of that structure and therefore the degree to which steric hindrance is lessened.

For further implications of this hypothesis and the necessary corollary that a sorbing solid is under strain, reference may be made to Chapter IV, pages 141 and 142, and to Chapter XIII.

INFLUENCE OF TEMPERATURE

Probably the greatest influence upon sorption is temperature. Dewar's work leads to the conclusion that, for the physical type of sorption, various gases and vapours are all sorbed to much the same extent, provided only that they are compared at corresponding temperatures that bear similar relations to their respective critical temperatures or boiling points. In practice this means an enormous difference between the sorption of different substances at any one absolute temperature. He found² that at the respective boiling points of liquid hydrogen, nitrogen and oxygen nearly the same volumes of each gas are sorbed by charcoal at atmospheric pressure; namely, 260 c.c. per gram. His data in table 3 show that

¹ See Chapter X, page 334.

² J. Dewar, *Proc. Roy. Inst. Gr. Brit.*, 1905, **18**, 183; *Ann. chim. phys.*, (8), 1904, **3**, 5.

this would presumably hold also for helium at its boiling point.

TABLE 3

Sorption of Helium and Hydrogen by 1 gm. of Charcoal at the Temperatures of Boiling and Solid Hydrogen

Temperature	Volumes of helium	Volumes of hydrogen
— 185° C. (boiling point of liquid air)	2.5	137
— 210° C. (liquid air under exhaustion)	5	180
— 252° C. (boiling point of liquid hydrogen)	160	258
— 258° C. (solid hydrogen)	195	—

The amount of helium sorbed by charcoal at room temperature has been shown by Miss Homfray¹ to be immeasurably small. At — 78° C. traces are sorbed, and at — 183° the amounts are just measurable.² On the other hand, sorption of a chemical type often persists up to extremely high temperatures, as, for example, the sorption of oxygen by platinum or tungsten at a white heat.

Recently Taylor³ has stressed the changes in the nature of sorption with change in temperature to which reference is made in Chapter I, page 9, including footnote 1, also page 10, including footnote 1, Chapter IV, pages 69, 120 and 121, and Chapter IX, pages 268, 278 (footnote 1), 310–316, 319 and 320, assembling also some unpublished personal communications as further illustrations. He assumes that all kinds of adsorption are potentially possible at all temperatures but that the more specific forms have so high a temperature coefficient that they take place at an appreciable rate and

¹ I. F. Homfray, *Z. physik. Chem.*, 1910, **74**, 129. However, Dewar (see table 2) obtained 2.5 c.c. per gram of charcoal, or fifteen volumes at the temperature of liquid air, and in a table referring to calorimetry indicated that two volumes were sorbed at 0° C. (*Proc. Roy. Inst. Gr. Brit.*, 1905, **18**, 182; *Compt. rend.*, 1904, **139**, 261).

² See also S. McLean, *Trans. Roy. Soc. Canada*, (3), 1918, **12**, 79.

³ H. S. Taylor, *J. Am. Chem. Soc.*, 1930, **52**, 5298; 1931, **53**, 578; H. S. Taylor and A. T. Williamson, *J. Am. Chem. Soc.*, 1931, **53**, 813; H. S. Taylor and A. Sherman, *J. Am. Chem. Soc.*, 1931, **53**, 1614. See also I. Masson, *Trans. Farad. Soc.*, 1928, **24**, 170. Also F. E. T. Kingman, *Nature*, 1931, **127**, 742; 1931, **128**, 272.

become observable only at higher temperatures and are termed "activated adsorption".

It is a novel assumption that adsorption upon a fully exposed surface may be of any degree of slowness. The writer regards the traditional view as possessing a greater measure of validity; namely, that adsorption upon a surface fully exposed to a gas is practically instantaneous, and that other reactions or processes, such as diffusion of the adsorbed molecule, are subsequent to its adsorption.¹ For example, when carbon monoxide is sorbed upon the mixed oxide, "hopcalite", it may be desorbed as such or it may in time react with the oxide to which it is attached, becoming carbon dioxide and then being removable as carbon dioxide, not, in general, as carbon monoxide. Reference should here be made to the discussion of the activation or electrification of desorbed gases, Chapter IX, pages 265-267. Here again the activation is exhibited subsequent to primary adsorption. Similarly, the formation of colloidal aggregates and crystals of silver upon glass² is subsequent to the original adsorption as a monatomic film.

It is of importance to note that neither the form nor the position of sorption isotherms undergoes any special change when experiments are carried out above and below the critical temperature of the gas.³

EFFECT OF TIME UPON THE VARIOUS FACTORS INVOLVED IN SORPTION

"The occurrence of absorption, or solid solution, is necessarily conditioned by the possibility of measurable diffusion. This has been shown to occur, for example, in charcoal at -180° , in palladium at ordinary temperatures, in gold and lead at moder-

¹ Professor H. S. Taylor in a private communication concurs in this point of view, but mentions the additional possibility that a molecule arriving from the gas phase may already possess sufficient energy to "go over right away into the activated form".

² J. Estermann, *Z. physik. Chem.*, 1923, **106**, 405; L. Hamburger, *Kolloid-Z.*, 1918, **23**, 177.

³ See for example, J. W. McBain and G. T. Britton, *J. Am. Chem. Soc.*, 1930, **52**, 2198, and many others.

ately raised temperatures, and in steel at high temperatures. It is hastened by rise of temperature, which may thus render it practically appreciable even where the true solubility may be lessened.

"On the other hand, adsorption rapidly diminishes with rise of temperature. It is also conditioned by the extent of surface, which is often small in the case of metals. The surface of metallic grains embedded in the interior of an alloy is only accessible through diffusion.

"For these reasons it seems plausible that occlusion phenomena in glasses and metals will be largely those of diffusion, of absorption, not so much of adsorption. Chemical reaction will also play a prominent part.

"These two phenomena, chemical reaction and solid solution, present but little mystery in themselves and sufficient criteria are available to identify them by experiment in any concrete case. The semi-quantitative behaviour of diffusion is also easily followed, although its quantitative mathematical expression is often complicated.

"One further point in the case of metals subjected to heat treatment is that processes which have occurred at higher temperatures sometimes become fixed on cooling on account of diffusion being practically inhibited at lower temperatures, and thus not allowing of any redistribution at the lower temperatures."¹

The effect of time is usually ignored except that a few hours or days are allowed for equilibrium to be attained, although it has been repeatedly shown that these equilibria may continue to be displaced to fresh values over very prolonged periods.

"True adsorption is nearly instantaneous. Any lag can at present be accounted for by the time required for the dissipation of the heat evolved or the comparative inaccessibility of a portion of the surface of a porous adsorbing agent."²

Probably the chief factor is the displacement of other materials such as impurities or solvent already sorbed or hindering access to the finer porosities.

"On the other hand, *absorption*, or solid solution, may be reasonably expected to obey Fick's diffusion law, which requires that it should commence with a very high velocity for the first

¹ J. W. McBain, *Trans. Farad. Soc.*, 1919, **14**, 203, 204.

² J. W. McBain, *Trans. Farad. Soc.*, 1919, **14**, 202.

few moments, but rapidly fall off with time, and theoretically require infinite time for perfect equilibrium to be attained.”¹

Chemical reaction, if it occurs, may present the most varied phenomena, particularly as reaction often proceeds vigorously in surface films as well as in solid solution. It is sometimes continuous, as in certain catalyses, and it is often overlaid by diffusion effects of the various reacting substances and their products.

A further complication is that diffusion is often not confined to solid solution but is taking place through the ultrapores or along the surfaces of ultrapores or other interstices. Here Fick's diffusion law could not be expected to apply. It is only when the solid is completely coherent and homogeneous that such diffusion equations as those developed by McBain² are strictly applicable. Activated charcoal, for example, is almost completely discontinuous (see the author's conception of “persorption”, Chapter IV, page 64). In a particular case a careful quantitative study can disentangle these processes even when several of them are simultaneously present, since they are to a certain extent independent and different in their nature and time relations. For example, in the experiments with iodine and charcoal,³ the amounts of iodine transported by diffusion processes extending over a number of years bore a relation to the concentration of the iodine solution which was that of the sorption formula and not that of solid solution; hence the process was not one of homogeneous solid solution but a transportation of iodine to slowly accessible ultrapores. This is in agreement with the experiments of Cude and Hulett⁴ on the time or extreme pressure required for liquids to penetrate charcoal. In passages approaching molecular dimensions diffusion of a dissolved substance such as iodine must be greatly retarded by the necessity for displacing an equal bulk of solvent as it goes

¹ J. W. McBain, *Trans. Farad. Soc.*, 1919, **14**, 202.

² J. W. McBain, *Z. physik. Chem.*, 1909, **68**, 471.

³ J. W. McBain, *Trans. Farad. Soc.*, 1919, **14**, 206.

⁴ H. E. Cude and G. A. Hulett, *J. Am. Chem. Soc.*, 1920, **42**, 391; H. C. Howard and G. A. Hulett, *J. Phys. Chem.*, 1924, **28**, 1082.

along. (See the discussion of the density of charcoal in Chapter IV, page 90.)

Another rather striking analysis of the different processes operating in sorption was made by the author, who studied the sorption of hydrogen by carbon at -183°C . and showed that it is easy to arrange that they are temporarily opposed; thus hydrogen may evolve from the surface of charcoal whose interior is still taking it up, or hydrogen may be temporarily adsorbed by charcoal whose interior has previously been super-saturated. These opposing operations are displayed in the corresponding reversals of the sign of the pressure changes with time.¹

For all these reasons there is no satisfactory general treatment of the whole field of sorption.

RATE OF SORPTION

The rate of sorption has received much experimental attention. It is extremely rapid in some cases as is illustrated by the fact that gas-mask charcoal exposed to air containing 7,000 parts of chloropicrin (CCl_3NO_2) per million sorbs 99.99 per cent of the chloropicrin in 0.03 seconds.² Active charcoal at the temperature of liquid air will sorb 100 times its own volume of air, reducing it from atmospheric pressure to a few millimetres in a few seconds. 20 gms. of charcoal at the temperature of liquid air will reduce the pressure in a vessel containing 2 litres from $1/50$ of an atmosphere to one three-millionth of an atmosphere in 19 minutes.³

¹ J. W. McBain, *Phil. Mag.*, (6), 1909, **18**, 916; *Z. physik. Chem.*, 1909, **68**, 471. For further experiments, see J. B. Firth, *Z. physik. Chem.*, 1914, **86**, 294; A. Pickles (*Chem. News*, 1920, **121**, 1), using ammonia and charcoal at room temperatures; B. Gustaver (*Kolloid-chem. Beihefte*, 1921, **15**, 259), using water vapour and Merck's animal charcoal; D. H. Bangham and F. P. Burt (*J. Phys. Chem.*, 1925, **29**, 120), using ammonia with glass wool.

² A. B. Lamb, R. E. Wilson and N. K. Chaney, *J. Ind. Eng. Chem.*, 1919, **11**, 420.

³ For numerical data see J. Dewar, *Proc. Roy. Inst. Gt. Brit.*, 1907, **18**, 750.

Perhaps the most successful studies of rate of sorption for particular cases are those of Bangham, Burt, Sever and Francis ¹ who studied the sorption of ammonia, carbon dioxide, sulphur dioxide and nitrous oxide by glass at approximately constant pressure. For the sorption, s , at any given time, t , they obtained the empirical expression, $s = x/m = kt^{1/n}$. This expression has the same form as the empirical sorption isotherm except that time is substituted for pressure or concentration. They found it to agree well with the data just quoted for the sorption of iodine by charcoal from solutions in benzene and toluene and with certain of the data of Bergter ² for the sorption of air by charcoal. It was confirmed by Herbert ³ for the sorption of gaseous ammonia by carborundum, and likewise by Bangham and Stafford ⁴ for the sorption of oxygen by graphite (under low pressures). They found a similar type of equation to govern the reverse process of desorption in its early stages, and fair agreement with many of Richardson's ⁵ data for the decay of positive ionization from hot wires was obtained by applying it in the differential form. The success of this purely empirical equation is illustrated in figs. 21 ⁶ and 22 ⁷ for the sorption of ammonia by glass. During the fourth week, as is seen in fig. 22, the rate of sorption begins a still further decline. This is only to be expected, for inspection of the empirical formula just given would

¹ D. H. Bangham and F. P. Burt, *Proc. Roy. Soc. (London)*, A, 1924, **105**, 481 ; *J. Phys. Chem.*, 1925, **29**, 113, 540 ; D. H. Bangham and W. Sever, *Phil. Mag.*, (6), 1925, **49**, 935 ; M. Francis and F. P. Burt, *Proc. Roy. Soc. (London)*, A, 1927, **116**, 586. However, M. Crespi and E. Moles (*Anales soc. españ. fis. quim.*, 1926, **24**, 452) found it necessary with sulphur dioxide and glass to use the formula

$$v = k[\log(t + 1)]^{2/5}.$$

² F. Bergter, *Ann. der Physik*, (4), 1912, **37**, 472.

³ J. B. M. Herbert (unpublished, quoted by Bangham and Sever, loc. cit.) ; see also *Trans. Farad. Soc.*, 1930, **26**, 118 (sodium chloride and alumina).

⁴ D. H. Bangham and J. Stafford, *J. Chem. Soc.*, 1925, **127**, 1085.

⁵ O. W. Richardson, *Phil. Mag.*, (6), 1904, **8**, 405.

⁶ D. H. Bangham and F. P. Burt, *J. Phys. Chem.*, 1925, **29**, 119.

⁷ D. H. Bangham and F. P. Burt, *J. Phys. Chem.*, 1925, **29**, 115.

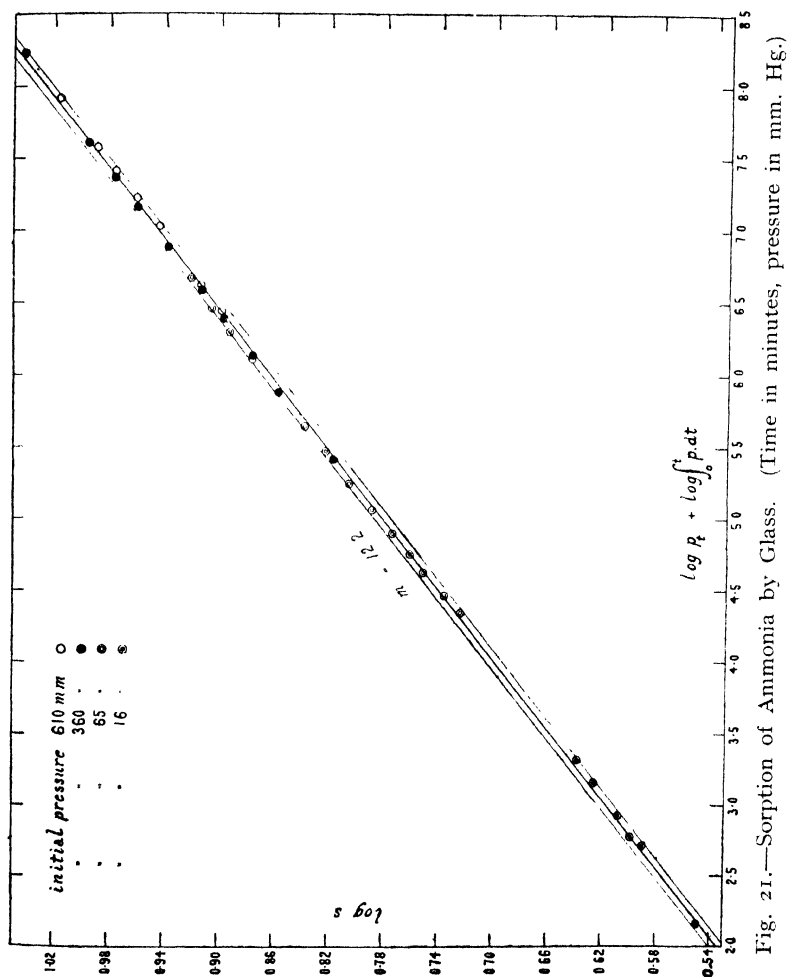


Fig. 21.—Sorption of Ammonia by Glass. (Time in minutes, pressure in mm. Hg.)

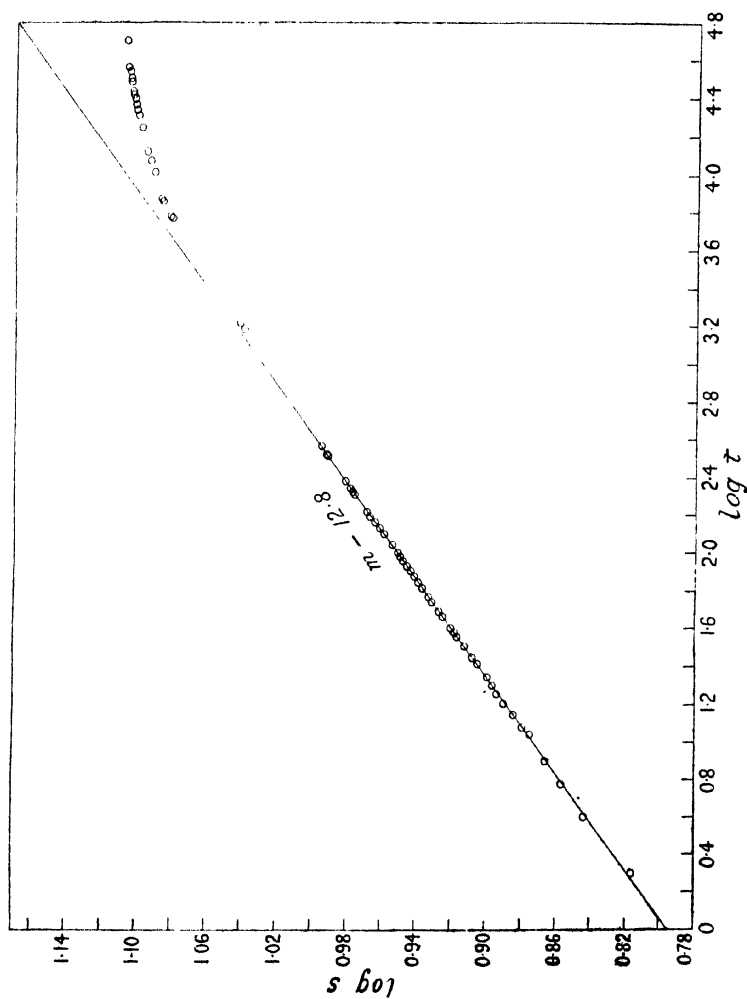


Fig. 22.—Sorption of Ammonia by Glass. (Time in Minutes.)

indicate an infinite amount of sorption at infinite time. For longer periods they, therefore, used the formula

$$\log \frac{\sigma}{\sigma - s} = kt^{1/n}$$

where σ is the estimated ultimate saturation value. This reduces to the preceding formula when the time is not too great.

If the glass is highly desiccated, the rate departs appreciably from the linear law, and the straight line becomes S-shaped. This formula assumes a formal resemblance to that of a reaction of the first order if $n = 1$ and is then identical with that used by Lagergren ¹ in his studies of the sorption of succinic acid by animal charcoal. This was used also by Blythswood and Allen ² for the sorption of air by charcoal. Dietl ³ showed that in these and similar formulæ, the value of k diminished with time. This is in agreement with the formulations of Iliin.⁴

The rate of sorption is doubled ⁵ for a rise of 20° C. Since sorption is frequently less at higher temperatures, it often happens that more sorption occurs in a short time at a higher temperature and that this is reversed for longer periods. Further, it is clear that the form of the sorption isotherm must depend upon the time.

The rate of sorption for a very large number of charcoals was found by Herbst ⁶ to be inversely proportional to the cube of the apparent density of the charcoal and also inversely proportional to the square root of the molecular weight of the gas. In other words, the rate is governed by the accessi-

¹ S. Lagergren, *Bihang t. K. Svenska Vet. Akad. Handl.*, 1898, **24**, Afd. II., No. 4; H. S. Harned, *J. Am. Chem. Soc.*, 1920, **42**, 372. Earlier studies of sorption are those of E. J. Mills and G. Thomson, *J. Chem. Soc.*, 1879, **35**, 26; E. J. Mills and J. Takamine, *J. Chem. Soc.*, 1883, **43**, 142.

² Lord Blythswood and H. S. Allen, *Phil. Mag.*, (6), 1905, **10**, 497.

³ A. Dietl, *Kolloidchem. Beihefte*, 1914, **6**, 127.

⁴ B. Iliin, *J. Russ. Phys. Chem. Soc., Physical Part*, 1924, **56**, 2.

⁵ M. Francis and F. P. Burt, *Proc. Roy. Soc. (London)*, A, 1927, **116**, 586.

⁶ H. Herbst, *Kolloidchem. Beihefte*, 1925, **21**, 1.

bility of the interior. Alekseevski ¹ found with charcoal that acetylene and benzene required half an hour to obtain equilibrium, whereas alcohol and acetic acid took twenty-four hours. Driver and Firth ² found the time required for equilibrium between the saturated vapours of such substances as carbon tetrachloride, benzene, ethyl propionate, ether, carbon disulphide, and toluene was between the fourteen days for chloroform and the two hundred days for methyl benzoate. Other studies on the rate of sorption of vapours by charcoal are those of Gustaver, ³ Tryhorn and Wyatt, ⁴ and Allmand, Chaplin, Shiels and Hand ⁵ with water vapour. Sameshima ⁶ has studied the rate of sorption by sugar charcoal with carbon dioxide and with ammonia, the latter over a period of six months; powdering the charcoal hastened the rate but did not affect the final amount sorbed. Rigorous evacuation enormously reduces the time required.

Mixtures are slower in arriving at equilibrium, and Lorenz and Wiedbrauck ⁷ show how the proportions vary with the time. Similarly, sorption is much hastened when the sorbing surface is thoroughly cleaned. The data of Harned ⁸ and Sheldon ⁹ illustrate the changes in the velocity laws during the course of the sorption of a gas by charcoal. Lemon ¹⁰

¹ E. V. Alekseevski, *J. Russ. Phys.-Chem. Soc.*, 1924, **55**, 401.

² J. Driver and J. B. Firth, *J. Chem. Soc.*, 1922, **121**, 2409.

³ B. Gustaver, *Kolloidchem. Beihefte*, 1921, **15**, 266.

⁴ F. G. Tryhorn and W. F. Wyatt, *Trans. Farad. Soc.*, 1926, **22**, 134.

⁵ A. J. Allmand, R. Chaplin and D. O. Shiels, *J. Phys. Chem.*, 1929, **33**, 1151; A. J. Allmand and P. G. T. Hand, *J. Phys. Chem.*, 1929, **33**, 1161.

⁶ J. Sameshima, *Bull. Chem. Soc. Japan*, 1927, **2**, 1; 1930, **5**, 173. See also the discussion by M. Tarlé, *Bull. Chem. Soc. Japan*, 1927, **2**, 243; J. Sameshima, *Bull. Chem. Soc. Japan*, 1927, **2**, 246.

⁷ R. Lorenz and E. Wiedbrauck, *Z. anorg. allgem. Chem.*, 1924, **135**, 42.

⁸ H. S. Harned, *J. Am. Chem. Soc.*, 1920, **42**, 372.

⁹ H. H. Sheldon, *Phys. Rev.*, (2), 1922, **19**, 253. A systematic study of rate of sorption of nitrogen and hydrogen with progressive heating and evacuation of the charcoal is contained in his previous paper (*Phys. Rev.*, (2), 1920, **16**, 165).

¹⁰ H. B. Lemon, *Phys. Rev.*, (2), 1919, **14**, 281.

has shown that the rate of sorption by activated coconut charcoal may be very greatly increased by repeatedly allowing it to sorb oxygen at a low temperature and evacuating at not over 650°C . Evacuation at higher temperatures diminished the rate and repeated treatment at lower temperatures restored it.

On fully exposed surfaces sorption is surprisingly quick. Thus, for example, sheets of mica will adhere when pressed together immediately upon cleaving them. The shortest delay suffices to prevent them from uniting. Similarly, Bridgman ¹ found that freshly exposed surfaces of iron prepared by breaking and immediately plunging them under mercury are not amalgamated. It is necessary to break the iron under mercury to bring about amalgamation of the new surfaces. Degen ² long ago published similar observations with regard to the wetting of such materials as slags by water.

Quincke ³ has collected a whole series of such interesting observations which are still as fascinating as ever and should not be forgotten, although now one might offer different explanations. Amongst the many facts adduced with regard to sorption upon surfaces as dependent upon their previous history are those of Degen ² and Faraday ² on ease of wetting, those of Biewend ⁴ on the conditions under which tiny spheres of gold and silver do or do not stick to each other and of Marcet ⁵ on the readiness with which liquids boil in contact with various glass and metal surfaces. Of particular interest are the numerous descriptions of the surprising and almost permanent impressions made upon surfaces by previous local experiences so that they may be made to reveal in actual picture the forms of bodies with which they have once come

¹ P. W. Bridgman, *Proc. Am. Acad. of Arts and Sciences*, 1911, **46**, 323.

² F. Degen, *Pogg. Ann. der Physik*, 1836, **38**, 449; see also M. Faraday, *Experimental Researches in Electricity*, 1839, **1**, 171 and 185, paragraphs 588 and 633.

³ G. Quincke, *Pogg. Ann. der Physik*, 1859, **108**, 326.

⁴ E. Biewend, *Pogg. Ann. der Physik*, 1842, **57**, 164.

⁵ F. Marcet, *Pogg. Ann. der Physik*, 1842, **57**, 218.

in contact or even approached.¹ These impressions may even be communicated to other surfaces.²

The rates of chemical reactions on different points of such surfaces may be very different either in direct reaction or in catalysis. The mechanism of photography by the daguerreo-type process depended upon such influences. Schroeder³ showed that after exposure to the air, metallic electrodes produce electrolytic currents until the effects are equalized. The passivity of metals is an extreme example.

Bhatnagar and Bhatia⁴ observed that the rates of evaporation of water from powdered iron, nickel and cobalt and the corresponding oxides were parabolic and in the same order as the values of Bohr's magneton for the respective metals and in inverse order to their magnetic susceptibility.

RELATION OF AMOUNT OF SORPTION TO PHYSICAL CONSTANTS

When sorption is of the distinctly physical type, general relations hold at least approximately with regard to the respective amounts of various substances that may be sorbed under similar conditions by a given material. The sorption is usually expressed for this purpose in cubic centimetres or number of molecules. These generalizations are all inter-related through such expressions as van der Waals' equation and critical data, but they are not exactly equivalent. The first, relating sorption to condensability of vapours, was pointed out in connexion with de Saussure's experiments in Chapter I, page 2. The second relation, which is another form of the first, connects sorption with the constant a of van der Waals' equation;⁵ see, for example, Chapter XVII, pages 457 and 458. Arrhenius⁶ compiled the following table

¹ E. Waidele, *Pogg. Ann. der Physik*, 1843, **59**, 255; L. Moser, *Pogg. Ann. der Physik*, 1842, **56**, 177; 1842, **57**, 1.

² H. Fizeau, *Pogg. Ann. der Physik*, 1843, **58**, 594.

³ H. Schroeder, *Pogg. Ann. der Physik*, 1841, **54**, 57.

⁴ S. S. Bhatnagar and S. L. Bhatia, *J. chim. phys.*, 1926, **23**, 545.

⁵ S. Arrhenius, *Medd. Vetenskapsakad. Nobelinst.*, 1911, **2**, No. 7, p. 24; *Theories of Solutions*, p. 55 (Yale University Press, New Haven, 1913).

⁶ S. Arrhenius, *Theories of Solutions*, p. 68.

from the data of Titoff and Miss Homfray for coconut charcoal at a pressure of 10 cm. Hg and 0° C. Miss Homfray's charcoal sorbed in general about 10 per cent less than that of Titoff. The sorption is expressed in cubic centimetres (measured at N.T.P.) per gram of charcoal. T_k is the critical temperature.

TABLE 4

Sorption of various Gases by Charcoal, showing Relation between Sorption, van der Waals' a , and critical Temperature

(Data of Titoff and Miss Homfray.)

Gas	$a \times 10^3$.	c.c.	T_k , ° abs.
Ethylene	8.83	41	284
Ammonia	8.08	71	403
Carbon dioxide	7.01	30	304
		28	
Methane	3.67	9.4	178
Carbon monoxide	2.80	3.2	133
Oxygen	2.69	2.5	155
Nitrogen	2.68	2.35	127
		2.0	
Argon	2.59	1.67	154
Hydrogen	0.42	0.227	32

The third relation is suggested by Schmidt¹ for all gases and vapours whose molecules are smaller than the average size of the pores in the solid. However, it should be borne in mind that the third generalization is almost the same as the first, because Trouton's rule connects boiling points with latent heats and the boiling point is two-thirds of the critical temperature.² The critical temperature, according to van der Waals, is equal to $\frac{8}{27} \frac{a}{bR}$. Schmidt's equation³ is that the logarithm of the amount of gas c sorbed by a porous body at one atmosphere pressure and at a given temperature chosen

¹ O. Schmidt, *Z. physik. Chem.*, 1928, **133**, 263.

² C. M. Knudson (*Dissert.*, State Univ. of Iowa, 1924) observed that three organic vapours, but not methylamine nor water, were similarly sorbed at corresponding temperatures.

³ Schmidt's formula is closely related to that of A. Eucken (*Verh. deut. physik. Ges.*, 1914, **16**, 348) (see Chapter XVII) and to the less determinate formula of Jaquet (Chapter XX).

between 0° and 150° C. is a linear function of the square root of the heat of vaporization λ .

$$\log c = k_1 \sqrt{\lambda} - k_2$$

where k_1 and k_2 are constants for each given sample of sorbing material. He has applied this formula to charcoal, chabasite, rubber, metallic powders, various oxides, silicic acid, dehydrated gypsum and even to the solubility of gases in alcohol and in water except where chemical interactions occur with the water. Examples of Schmidt's results are given in fig. 23.¹

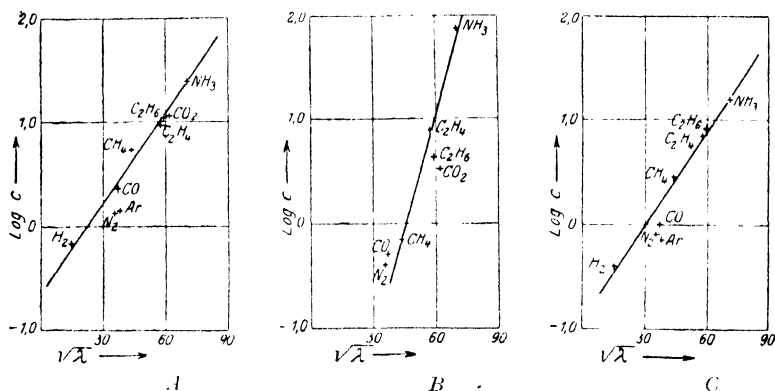


Fig. 23.—Sorption of Gases and Vapours by Charcoal graphed according to Schmidt's Equation, $\log c = k_1 \sqrt{\lambda} - k_2$.

A.—Silica at 100° and 760 mm.

B.—Charcoal at 20° and 760 mm.

C.—Charcoal at 50° and 760 mm.

Eucken² relates adsorption potential to the square root of the absolute boiling point, the square root of van der Waals' constant a , and to the square root of the latent heat of vaporization.

Lorenz and Landé,³ like Magnus,⁴ confine the strict com-

¹ O. Schmidt, *Z. physik. Chem.*, 1928, **133**, 292, figs. 4, 5 and 6.

² A. Eucken, *Z. Elektrochem.*, 1922, **28**, 12.

³ R. Lorenz and A. Landé, *Z. anorg. allgem. Chem.*, 1922, **125**, 47.

⁴ A. Magnus, *Z. anorg. allgem. Chem.*, 1926, **158**, 67; etc.

parison of the isotherms for various substances to the regions of pressure and temperature where Henry's law applies.

A relation which has been lost sight of in recent years is that between the solubility of gases and vapours and the readiness with which they are sorbed (compare Chapter XII, page 377). This is almost the opposite of the well-known rule of sorption from solutions, where the less soluble substances are most readily extracted by sorption. Sulphur dioxide and ammonia are more readily sorbed than nitrogen or hydrogen, probably for exactly the same reason that they are more soluble in water. The laws of interaction are common to chemistry and physics. For an exact parallelism with sorption, solubility in a solvent of similar chemical constitution should be taken for comparison.

CHAPTER IV

SORPTION BY CHARCOAL

" ACTIVE " CHARCOAL

Sorption by charcoal depends to a very great extent upon the source as well as upon the preliminary treatment of the charcoal. The importance of industrial applications and the use of charcoal in gas masks in chemical warfare has led to the development of an extensive literature on methods of increasing the sorbing capacity of various charcoals. These processes, some very old,¹ but mostly subsequent to 1910, are termed " activation ". The term active charcoal is, however, rather loosely applied. The activated charcoals may be of the most varied origin, animal or vegetable. Wood, peat and lignite are common examples. Kausch² lists over 300 references to the literature. A brief recent summary of German patents is that of Bräuer and Reitstötter.³

The older forms of gas-mask charcoal from German, English and American sources have been compared by Lowry and Hulett.⁴ The Dutch active charcoals, " Norit " and " Supra-Norit ", are made from hard woods such as beech or sometimes from anthracite or even fruit stones and pips. The

¹For example, J. Stenhouse (*Chem. Zentr.*, 1857, **28**, 64 (from *Polytech. Centr.*, 1856, p. 77) and 353 (from *Ann. der Chem. und Pharm.*, **101**, 243)) impregnated charcoal with calcium phosphate or aluminium or iron salts before ignition and made another excellent decolorizing charcoal by impregnating pitch with calcium hydroxide and extracting after ignition.

²O. Kausch, *Die Aktive Kohle ihre Herstellung und Verwendung, Monographien über chemische-technische Fabrikationsmethoden*, 1928, **42**, 1-342. Wilhelm Knapp, Halle.

³A. Bräuer and J. Reitstötter, *Z. angew. Chem.*, 1928, **41**, 536.

⁴H. H. Lowry and G. A. Hulett, *J. Am. Chem. Soc.*, 1920, **42**, 1393, 1408.

charcoal is ground and briquetted and held together by hardening agents. It is activated chiefly by highly superheated steam with simultaneous partial oxidation and subsequent heating at a very high temperature, even above $1,100^{\circ}\text{C}$. Sugar charcoal does not carry the reputation of being more than moderately active, but it has been shown in the writer's laboratory, at both Stanford and Bristol Universities, that sugar charcoal may be made fully as active as any other charcoal.

The activating agents and processes are likewise varied. Methods of activation always involve heating to more or less elevated temperatures which may range from 350°C . to $1,150^{\circ}\text{C}$. Part of the charcoal itself is always lost, and the increase in the activity is usually parallel with this loss. Heating to $1,000^{\circ}\text{C}$. in an inert atmosphere of helium or nitrogen or in vacuo causes partial gasification of any charcoal that has been previously exposed to air at room temperature, whether it has been activated or not, and results in a notable increase in activity.¹ Similarly, Herbst² found that heating to not over $1,150^{\circ}\text{C}$. increased sorptive capacity, whereas heating to higher temperatures was deleterious.

Mere heat does not impair active carbon, at least up to about $1,000^{\circ}\text{C}$.³ Herbst measured the electrical conductivity

¹ Experiments in the writer's laboratory by Drs. F. Carlyle Harmon and R. F. Sessions. H. H. Sheldon (*Phys. Rev.*, (2), 1920, **16**, 170) asserts that even the slow oxidation on standing at room temperature for four years activates charcoal. H. B. Lemon (*Phys. Rev.*, (2), 1919, **14**, 281) found that an effective method of activation is repeated sorption of oxygen at the temperature of liquid air followed each time by evacuation at not over 650°C .

² H. Herbst, *Biochem. Z.*, 1921, **115**, 214.

³ H. H. Lowry, *J. Phys. Chem.*, 1930, **34**, 63. However, the experiments of A. Magnus and H. Kratz (*Z. anorg. allgem. Chem.* 1929, **184**, 252) on heating 48 specimens of charcoal for very prolonged periods at temperatures up to $1,000^{\circ}$, in the latter case in a graphite crucible embedded in charcoal, otherwise in fused silica, may well have been affected by graphitization; their optimum temperature was 800°C . A similar decrease was obtained in a similar experiment by O. Ruff, S. Mugdan, E. Hohlfield and F. Feige, *Kolloid-Z.*, 1923, **32**, 230 (800° to $1,410^{\circ}\text{C}$.); after heating one half-hour at $1,400^{\circ}$, the charcoal

of powdered charcoal after heating in order to test the progress of graphitization. The current obtained rose from 0.004 milliamperes, after heating at 700° C., to 1.6 after 900° C., 35 after 1,100° C., and 310 after 1,300° C.

Treatment with superheated steam at temperatures between 800° and 1,000° C. is a common mode of activation. Impregnation with zinc chloride and heating above 300° C. was employed in making German gas-mask charcoal. It is used for preparing certain industrial active charcoals such as "Carboraffin". Treatment with one of the halogens and subsequent heating is sometimes employed. Other impregnating agents are phosphoric, sulphuric or organic acids, or alkalies.

As an example of activation by chlorine with subsequent heating, the data of Winter and Baker ¹ for sugar charcoal may be quoted. After four hours at 900°, its apparent density was 1.76 which rose to 1.84 at 40 hours. The former sorbed at 0° 97 c.c. of sulphur dioxide per gram and the latter 195 c.c. A further 5½ hours' heating raised this to 288 c.c. They compare these values with those of de Saussure ² and of Favre ³ who both used charcoal of apparent density 1.57, one gram of which sorbed 41 ⁴ and 105 c.c. of sulphur dioxide, respectively.

The commonest and sometimes the most effective method of activating charcoal is to heat it in a restricted current of air so that a portion is slowly oxidized. Lamb, Wilson and Chaney ⁵ and their associates state that the optimum temperature lies between 350° and 450° C. However, it has been

sorbed half as much phenol as after heating at 800° C. With exceptionally pure charcoal (99.7-99.8 per cent carbon) the optimum temperature was 1,000° C. as shown by sorption of carbon dioxide (G. I. Chufarov, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 883).

¹ R. M. Winter and H. B. Baker, *J. Chem. Soc.*, 1920, **117**, 319.

² T. de Saussure, *Gilbert's Ann. der Physik*, 1814, **47**, 113; *Ann. Phil.*, 1815, **6**, 241, 331.

³ P. A. Favre, *Ann. chim. physik*, (5), 1874, **1**, 244.

⁴ Thirty-eight as quoted by Winter and Baker.

⁵ A. B. Lamb, R. E. Wilson and N. K. Chaney, *J. Ind. Eng. Chem.*, 1919, **11**, 420.

shown in the writer's laboratory that instead of air activation being practically confined to this narrow optimum range of temperature, redwood and sugar charcoals may be even more advantageously air-activated at far higher temperatures. Air activation can therefore be carried out at any temperature between 350° and $1,150^{\circ}$ C. The two optimum temperature regions are near the two limits of this range. For example, the highly active sugar charcoal prepared by H. G. Smith¹ with iodine value (see later) equal to 85 per cent was thus prepared at $1,140^{\circ}$ C.

Different kinds of active charcoal are prepared for different purposes. Granular forms are required for the sorption of gases and vapours or in gas masks; fine powders for use in liquids such as oils, fats, wine, sugar, glycerine, or organic acids for bleaching and decolorizing; or for medicinal purposes such as, for example, in digestive disorders or in such diseases as typhus. Some are used for catalyses, such as the manufacture and decomposition and hydrolysis of phosgene and other war gases, ethylene dichloride and sulphuryl chloride, the oxidation of chlorine by steam to form hydrogen chloride, or the oxidation of hydrogen sulphide by air to form sulphur and water vapour. A good summary of the industrial and therapeutic applications of various charcoals and other solids has been given by Krczil.² A number of active charcoals are described by Herbst.³ As Mecklenburg⁴ points out,

¹ J. W. McBain, D. N. Jackman, A. M. Bakr and H. G. Smith, *J. Phys. Chem.*, 1930, **34**, 1439.

² F. Krczil, *Untersuchung und Bewertung technischer Adsorptionsstoffe*, pp. 261-469 (Akademische Verlagsgesellschaft, m.b.H., Leipzig, 1931).

³ H. Herbst, *Kolloidchem. Beihefte*, 1925, **21**, 1.

⁴ W. Mecklenburg, in R. E. Liesegang, *Kolloidchemische Technologie*, Aktive Kohle, pp. 969-978 (Th. Steinkopff, Dresden and Leipzig, 1927). M. M. Dubinin (*Z. physik. Chem.*, Abt. A, 1930, **150**, 145; *J. Russ. Phys. Chem. Soc.*, 1929, **61**, 587) even finds that a sugar charcoal, heated or air activated at various temperatures, is improved for one particular kind of sorption whilst being less improved or even impaired for others (see *Chemical Abstracts*, 1929, **23**, 2536; 1930, **24**, 282 for interesting details).

activated charcoals are sufficiently specific that one that is good for one purpose may not be suitable for others.¹

Methods² of testing charcoals and other solids for their activity or sorbing power may be very briefly referred to here.

There are five main methods of testing charcoals for their activity, though each method has numerous modifications introduced by different workers.

(1) Briefly, the colour method consists in shaking up the charcoal (dried at 120° C.) with a 0.15 per cent solution of dye. After centrifuging or filtering, the dye is abstracted and the amount sorbed per minute is estimated by such methods as colour change, titration with crystal Ponceau 6R, titanous chloride or iodine and thiosulphate. The dyes used are methylene blue, indigo, bismarck brown and crystal violet.

(2) The second chief method consists of shaking up one gram of the charcoal in 100 c.c. of either 1 per cent or 0.2 N iodine solution for three minutes and estimating the iodine sorption by thiosulphate titration. Organic solvents can be used for extraction.

(3) In the third method, mercuric chloride is used. An excess is added and the amount not sorbed is estimated interferometrically, by analysis or by titration with potassium cyanide.

(4) Phenol is easily sorbed by charcoal, and the activity is measured directly by the amount taken up during shaking for a definite time. The phenol not sorbed is estimated titrimetrically or by the interferometer.

¹ A good example of this is afforded by the exceptionally pure charcoal (99.7 to 99.8 per cent carbon) prepared by decomposing piperonal in an autoclave at 200°–210° C. and 18 to 20 atmospheres pressure (G. I. Chufarov, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 883). This sorbs carbon dioxide strongly but phenol from solution only to an insignificant extent. Heating above 500° C. improves it for sorption of carbon dioxide but greatly diminishes the sorption of phenol. Activation does not affect its sorption of carbon dioxide but gives it high sorbing power towards phenol.

² There is a good summary of the various methods and their practical details in a monograph by F. Krczil entitled *Untersuchung und Bewertung technischer Adsorptionsstoffe*, pp. 206–260 (Akademische Verlagsgesellschaft, m.b.H., Leipzig, 1931).

(5) Benzoic acid is also often used in estimating activities. In this case the charcoal is first evacuated by a water pump and after shaking 24 hours the non-sorbed benzoic acid is titrated with sodium hydroxide.

Water has also been used for activity estimation. Charcoal is dried to constant weight and left in an exsiccator containing pure water. Water vapour is taken up and the amount is estimated by weighing to constant weight.

Macy¹ found the heat of wetting of benzene by charcoal to be proportional to the retentivity (that is, the initial slope of the isotherm) of the charcoal for the vapour. He therefore uses this as a method of activity measurement and lists data for seventeen charcoals to illustrate the relationship. His values are reproduced in table 5.

TABLE 5

Relation between Heat of Wetting in Benzene, Maximum Adsorption of Saturated Benzene Vapour, and Retentivity of Benzene at 25° C.

Charcoal	Apparent density	Heat of wetting cal./g.	Maximum adsorption mg./g.	Retentivity	
				mg./g.	mg./c.c.
Wood charcoal .	0.29	2.4	26	14	4
Norit .	0.19	15.8	367	137	26
Batchite* .	0.78	5.1	129	48	37
Pine † .	0.24	20.8	496	142	34
Oak † .	0.44	11.4	206	128	56
Ironwood † .	0.40	13.5	206	135	54
German ‡ .	0.29	19.6	655	136	40
Coal briquets § .	0.42	14.3	354	135	57
Urbain .	0.25	25.2	780	258	65
Ironwood † .	0.45	14.5	227	150	68
Maple † .	0.26	25.4	560	234	61
Oak † .	0.44	17.5	307	184	81
Ironwood † .	0.47	14.9	244	148	70
Oak † .	0.35	23.4	437	233	82
Oak † .	0.32	27.5	623	310	99
Oak † .	0.42	23.6	486	263	110
Coconut § .	0.48	23.0	371	231	111

* The generic name for steam activated anthracite coal.

† Activated with carbon dioxide.

‡ Activated with zinc chloride.

§ Activated with steam.

¹ R. Macy, *J. Phys. Chem.*, 1931, **35**, 1397.

Charcoals are often tested for the amount of carbon tetrachloride which they can sorb or for their retentivity towards chloropicrin. It is always best to test charcoals directly with the materials for which they are designed.

All modes of activation seem to consist in the removal of material in contact with the atoms of carbon, chiefly by oxidation. Such material may be hydrocarbons, tar, films of oxide, or portions of the carbon chains themselves. Even mere heating in vacuo involves expulsion of large amounts of the oxygen inevitably present, which will come off as a mixture of carbon monoxide and dioxide.¹ The result is the opening and exposing of the fine structure of the charcoal, often down to molecular or atomic dimensions. This allows almost complete permeation by molecules which are not too large. It is evident that the conception of ordinary surface disappears when one speaks of the surfaces of the individual exposed atoms, whilst on the other hand the complete homogeneity of a solid solution is not attainable. For these reasons the author has proposed² rejection of the term adsorption as applied to such highly active charcoal, preferring to call it "persorption" or merely sorption.

¹ J. Driver and J. B. Firth (*J. Chem. Soc.*, 1922, **121**, 2409) showed that heating in vacuo for 48 hours at 900° C. (or lower temperature) increases by as much as two-fold the sorptive capacity of animal charcoal, sugar charcoal and lamp black, as tested with chloroform and with benzene. However, heating in vacuo for 12 hours at 1,000° C. reduced the sorptive capacity below that at 6 hours except for lamp black (their most efficient charcoal) and even with lamp black further heating in vacuo at 1,000° reduced the sorption. O. Ruff and G. Roesner (*Ber.*, 1927, **60**, 415) give the following table for the "activity" (towards solutions of phenol) and the sorbing capacity in cubic centimetres at 0° and 700 mm. Hg of Supra-Norit previously activated at 900° in a current of carbon dioxide and then heated in vacuo or in an indifferent gas:—

Temp. ° C.	Activity %	Argon. Cubic Centimetres	CO ₂ .	NH ₃ .
900	55	12.75	81	274
1500	40	—	71.3	—
2000	23	6	38	105
2700	2	1.3	5	12.6

² J. W. McBain and G. T. Britton, *J. Am. Chem. Soc.*, 1930, **52**, 2198. Compare Chapter V.

It is clear why pulverizing the lumps of charcoal has no great effect upon the amounts of gases of low molecular weight which can be sorbed. In most cases there may be a slight increase ¹ but occasionally there is a decrease ² which Freundlich ³ ascribes to crushing of pores hindering access by diffusion. Baerwald,⁴ for example, found that powdering the extremely voluminous elder pith charcoal thus greatly lowered its sorptive capacity for gases.

Lamb, Wilson and Chaney ⁵ state that active charcoal can be obtained only from carbon formed or deposited at relatively low temperatures.⁶ It is then coated with a complex of

¹ H. Violette (*Ann. chim. phys.* (3), 1853, **39**, 291) observed that powdered charcoal sorbs twice as much water vapour as lump charcoal.

² T. de Saussure, *Gilbert's Ann. der Physik*, 1814, **47**, 113; *Ann. Phil.*, 1815, **6**, 241, 331; H. Baerwald, *Ann. der Physik*, (4), 1907, **23**, 84.

³ H. Freundlich, *Colloid and Capillary Chemistry*, p. 132. Methuen & Co., London, 1926.

⁴ H. Baerwald, *Ann. der Physik*, (4), 1907, **23**, 84.

⁵ A. B. Lamb, R. E. Wilson and N. K. Chaney, *J. Ind. Eng. Chem.*, 1919, **11**, 420.

⁶ W. Hempel and G. Vater (*Z. Elektrochem.*, 1912, **18**, 724) found 600° C. the optimum temperature for preparing coconut or ox-blood charcoal. T. Okazawa (*Bull. Inst. Phys. Chem. Research* (Tokyo), 1928, **7**, 821; English Ed., **1**, 75) found that charcoals heated to 300° and 500° were similar as regards sorption of water, benzene or alcohol vapour. If the charcoal is not to be subsequently activated, carbonization ought to be carried out at a much higher temperature (H. E. Watson, *J. Soc. Chem. Ind.*, 1919, **38**, 99R; K. Scheringa, *Pharm. Weekblad*, 1920, **57**, 348). Coconut charcoal carbonized at as low a temperature as possible and then heated to 600° exhibits considerable increase in sorptive power without material increase in density. At 900° a much greater increase is obtained coincident with a marked increase in density (J. B. Firth, *J. Chem. Soc.*, 1921, **119**, 926). H. B. Lemon (*Phys. Rev.*, (2), 1919, **14**, 281), on the contrary, stated that heating coconut charcoal which was already air activated to 900° was deleterious, at least to rate of sorption; and after heating to 1,200° C. in quartz or iron, the rate became negligible. J. C. Philip and J. Jarman (*J. Phys. Chem.*, 1924, **28**, 346), using 25 samples of birch-wood charcoal carbonized at different temperatures from 350° to 850° for varying times, analysed them for carbon, hydrogen and ash and tested their adsorptive power in relation to iodine, oxalic acid, methylene blue, tartar emetic and quinine sulphate and came to

hydrocarbons stabilized by sorption.¹ Likewise, Chaney and Ray² consider that carbon liberated below 600° or 700° C. is active, whereas any formed above is inactive, and, moreover, cannot be activated. For example, that from carbon monoxide by catalysis with ferrous oxide at 300° is active; the carbon from carbon tetrachloride with mercury³ or sodium amalgam⁴ is active; that from cracking of methane at high temperatures is inactive. Hence they maintain that it is essential in activating charcoal to avoid decomposition of the hydrocarbons in such manner as to deposit a coating of inactive carbon upon the surface.⁵ Ray illustrates this for activated coconut charcoal held at 1,000° C. in a current of natural gas; during two hours its sorbing power for toluol under arbitrary conditions was reduced from 22 to 6. Hartmann and Dossmann⁶ prepared deposits of crystalline carbon by

the conclusion that the optimum temperature for the production of a charcoal by carbonization alone depended on the nature of the substance to be sorbed. H. Violette (*Ann. chim. phys.*, (3), 1853, **39**, 291), studying charcoal from 72 different kinds of wood, found that the quantity of water sorbed from humid air diminished with increasing temperature of carbonization between 150° and 1,500°, being 21, 7, 4 and 2 per cent at 150°, 250°, 430° and 1,500°, respectively. O. Ruff and H. Backe agree with Lamb, Wilson and Chaney (*Kolloid-Z.*, 1926, **38**, 59). They investigate systematically the effect of various factors upon the final activity of the charcoal.

¹ N. K. Chaney, *Trans. Am. Electrochem. Soc.*, 1919, **36**, 91.

² N. K. Chaney, *Trans. Am. Electrochem. Soc.*, 1919, **36**, 91; N. K. Chaney, A. B. Ray and A. St. John, *Ind. Eng. Chem.*, 1923, **15**, 1244; A. B. Ray, *Chem. Met. Eng.*, 1923, **28**, 977.

³ G. Tammann, *Z. anorg. allgem. Chem.*, 1921, **115**, 145.

⁴ B. Fetkenheuer, *Z. anorg. allgem. Chem.*, 1921, **117**, 281.

⁵ A. B. Ray, *Chem. Met. Eng.*, 1923, **28**, 977. See also O. Ruff, *Kolloid-Z.*, 1926, **38**, 174; O. Ruff and E. Hohlfeld, *Kolloid-Z.*, 1924, **34**, 135. G. A. Brender à Brandis (*Het Gas*, 1924, **44**, 5) points out that if active carbon (formed below 500° C.) is allowed to sorb a large quantity of hydrocarbons, its sorbing capacity cannot be restored by simple heating, since up to 500° C. the hydrocarbons are not given off and at higher temperatures form inactive carbon. See also R. Adler, *Patents J.*, October, 1923, 4646.

⁶ C. A. Hartmann and H. Dossmann, *Z. tech. Physik*, 1928, **9**, 434. Compare U. Hofmann, *Ber.*, 1928, **61B**, 1180, 2183; K. A. Hofmann and U. Hofmann, *Ber.*, 1926, **59B**, 2433; K. A. Hofmann and C.

heating hydrocarbons in a vacuum furnace at 600° to 1,000°. The particles were 130 to 1,300 atomic diameters thick and possessed a specific gravity of 2.04 to 2.07, as measured in water.

Chaney,¹ Herbst² and Ruff³ concur in regarding the sorbing carbon as amorphous or "paracrystalline", not graphitic. Nor has it the crystalline structure of diamond. When lines are observed in X-ray examinations, they correspond to the space lattice of graphite,⁴ although Chaney, Ray and St. John state that active charcoal when strongly heated gives a "pseudo graphite" distinctly modified from graphite. Lowry,⁵ in contrast to Chaney, considers that the fact that the sorptive power parallels the hydrogen content shows that

Röchling, *Ber.*, 1923, **56B**, 2071; E. Koch-Holm, *Wiss. Veröffentlich. Siemens-Konz.*, 1927, **6**, 188.

¹ N. K. Chaney, *Trans. Am. Electrochem. Soc.*, 1919, **36**, 91.

² H. Herbst, *Kolloidchem. Beihefte*, 1925, **21**, 1.

³ O. Ruff, *Z. angew. Chem.*, 1925, **38**, 793; *Kolloid-Z.*, 1926, **38**, 174.

⁴ P. Debye and P. Scherrer, *Physik. Z.*, 1917, **18**, 291; G. Asahara, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), 1922, **1**, 23; *Japan. J. Chem.*, 1922, **1**, 35; N. K. Chaney, A. B. Ray and A. St. John, *Ind. Eng. Chem.*, 1923, **15**, 1244; H. C. Howard and G. A. Hulett, *J. Phys. Chem.*, 1924, **28**, 1082; O. Ruff, G. Schmidt and W. Olbrich, *Z. anorg. allgem. Chem.*, 1925, **148**, 313; G. L. Clark, *Ind. Eng. Chem.*, 1926, **18**, 1131; Colloid Symposium Monograph (*Massachusetts Inst. Tech.*, 1926), 1926, **4**, 155; S. S. Pickles, *Trans. Inst. Rubber Ind.*, 1926, **2**, 85; H. H. Lowry and R. M. Bozorth, *J. Phys. Chem.*, 1928, **32**, 1524; U. Hofmann, *Ber.*, 1928, **61B**, 1180; W. G. Wykoff (N. Goodwin and C. R. Park), *Ind. Eng. Chem.*, 1928, **20**, 622; I. Ogawa, *Biochem. Z.*, 1926, **172**, 249; P. G. T. Hand and D. O. Shiels, *J. Phys. Chem.*, 1928, **32**, 454; M. E. Barker, *Ind. Eng. Chem.*, 1930, **22**, 928. See also footnote 6 on page 66 of this chapter. On the other hand, S. Paramasivan (*Indian J. Physics*, 1929, **4**, 142) finds that the specific diamagnetic susceptibilities of charcoals from naphthalene, anthracene, sugar, coal gas, wood charcoal and two kinds of coal were all close to that of diamond (0.5×10^{-6}), while that of graphitic anthracite is 0.97×10^{-6} and that of graphite itself is 4.2×10^{-6} . M. Hirata (*Sci. Papers Inst. Phys. Chem. Research* (Tokyo), 1930, **14**, 71) found that the patterns from activated coconut charcoal with sorbed organic liquids were not identical with that of the charcoal and liquids separately.

⁵ H. H. Lowry, *J. Am. Chem. Soc.*, 1924, **46**, 824; H. H. Lowry and S. O. Morgan, *J. Phys. Chem.*, 1925, **29**, 1105.

this so-called amorphous carbon is really unsaturated hydrocarbon of low hydrogen content. Lenher,¹ having shown that pure carbon in its various forms does not react with selenium oxychloride even when heated to moderate temperatures, demonstrates by extracting "retorted nut shells" with selenium oxychloride that the essential difference between "retorted" carbon and "activated" carbon is due to the presence of hydrocarbons thus removed. After such extraction at the ordinary temperature and subsequent removal of the selenium oxychloride and extractive matter, the carbon then shows the same sorptive properties toward such substances as chloropicrin as does the carbon which has been activated by the action of steam at high temperatures. Lemon² found a loss in efficiency after extraction with ligroin, alcohol or acetone. Netzke³

"found that bromine was adsorbed by substitution in untreated carbon blacks. After heat activation, the same amount of bromine was adsorbed, but in this case as an addition product. He therefore concluded that activation is a process of increasing the unsaturated condition of the charcoal substance."

Charcoal shrinks above 900° and tends to lose activity, and X-ray examination shows it to be completely graphitized by 2,400° C.

Howard and Hulett⁴ found that heating for one hour in vacuo at 1,100° to 1,200° decreases the sorptive power of coconut charcoal for nitrogen by one-half. They adduce the following data:

Temperature ° C.	Density (specific gravity measured with helium)	Sorption of N ₂ , c.c. (at N.T.P.) per g.
900-1,000 . . .	2.22	8.2
1,100-1,200 . . .	2.26	3.9
1,300-1,400 . . .	2.13	3.8
Approx. 1,600 . . .	1.44	0.2
Approx. 2,000 . . .	1.35	0.2

¹ V. Lenher, *J. Am. Chem. Soc.*, 1922, **44**, 1664.

² H. B. Lemon, *Phys. Rev.*, (2), 1919, **14**, 281.

³ Netzke, Report 3, Problem W-2, *Mass. Inst. Tech.*; through M. E. Barker, *Ind. Eng. Chem.*, 1930, **22**, 926.

⁴ H. C. Howard and G. A. Hulett, *J. Phys. Chem.*, 1924, **28**, 1092.

For a discussion of the significance of these densities see page 92 of this chapter (see also page 103).

In practice one distinguishes two kinds of amorphous charcoal or carbon, active and inactive. Part of the difference is due to the fact that the carbon of inactive samples is coated with hydrocarbons or tarry material.¹ Lamb, Wilson and Chaney² state that the sorptive powers of an active amorphous carbon can be ruined by the deposition of a thin film of graphitic carbon. Oxidation is also probably necessary, and indeed is unavoidable. Lowry and Hulett³ found that oxygen can be removed by evacuation to the extent of about 50 per cent at room temperature but only in traces at 184°. Only above 900° may such oxygen be removed and then only as a mixture of carbon dioxide and carbon monoxide. Even so it is not completely removable until 1,180° C.; above that temperature, hydrogen is collected. If subsequently the charcoal is exposed to hydrogen or oxygen at more ordinary

¹ H. Briggs (*Proc. Roy. Soc. (London)*, A, 1921, **100**, 88) reasons that this is inadequate as a complete explanation, because the amount is small in proportion to the effect, oxidation is essential, and expulsion of the hydrocarbons would require 1,000°, whereas 400° was regarded by Lamb, Wilson and Chaney to be an optimum for activation.

² A. B. Lamb, R. E. Wilson and N. K. Chaney, *J. Ind. Eng. Chem.*, 1919, **11**, 420.

³ H. H. Lowry and G. A. Hulett, *J. Am. Chem. Soc.*, 1920, **42**, 1408. References are there given to the literature on the numerous known complexes of high carbon and low oxygen content. I. Langmuir (*J. Am. Chem. Soc.*, 1915, **37**, 1154) has found a very stable complex on graphite, not decomposing until between 1,425° and 1,925° C. K. A. Kobe (*J. Chem. Educ.*, 1931, **8**, 232) presents an interesting and concise account of the four oxides of carbon other than carbon dioxide and carbon monoxide; namely, C_3O_2 , C_5O_5 , C_6O_6 and $C_{12}O_9$, together with their structural formulæ as determined from the organic chemicals to which they are related, referring also to the three modes suggested by N. Shilov, H. Shatunovska and K. Chmutov (*Z. physik. Chem.*, Abt. A, 1930, **149**, 211) for the attachment of oxygen to the surface atoms of carbon. See also L. H. Reyerson and K. Kobe, *Chem. Reviews*, 1930, **7**, 479.

temperatures, the oxygen is again fixed, whilst the hydrogen is easily recoverable.¹

Thus it is a mistake to think of charcoal as pure carbon.² It contains much oxygen and hydrogen, both very firmly held (*vide* tables 10 and 11 *infra*). Indeed Lowry³ has shown that the amount of hydrogen retained is chiefly dependent upon the highest temperature to which the charcoal has been exposed, being 0.5 per cent at 900° or 1,000° and 0.15 or 0.2 per cent at 1,200°.

Zinc chloride activated charcoal may contain 8 per cent oxygen, 2.2 per cent hydrogen and only about 86 per cent carbon; whereas steam and air activated charcoals may contain as much as 97 or 98 per cent of carbon. Some of the latter tend to be pyrophoric,⁴ whilst the former are not.

¹ H. B. Lemon (*Phys. Rev.*, (2), 1917, **9**, 337) states that on evacuation of coconut shell charcoal, "nitrogen comes out freely at temperatures as low as 150°, the rush of oxygen begins at 300° and is greatly augmented again at 600°". "At 900° hydrogen dominates." A. J. Allmand, R. Chaplin and D. O. Shiels (*J. Phys. Chem.*, 1929, **33**, 1153) confirm these observations. They determined the amounts of nitrogen, carbon dioxide, carbon monoxide, oxygen and hydrogen obtainable from charcoal at 270° to 800° C. See also A. J. Allmand and P. G. T. Hand, *J. Phys. Chem.*, 1929, **33**, 1163; A. J. Allmand and R. Chaplin, *Proc. Roy. Soc. (London)*, A, 1930, **129**, 235, 252. C. R. Johnson (*Ind. Eng. Chem.*, 1929, **21**, 1288) obtained from carbon black above 400° C. hydrogen, carbon monoxide, carbon dioxide and a very small amount of oxygen; it was noteworthy that carbon black on heating at low pressure lost less weight than at higher pressure, because there was more hydrogen, more oxygen, and less carbon monoxide and carbon dioxide evolved. M. E. Barker (*Ind. Eng. Chem.*, 1930, **22**, 926) found that the proportion of hydrogen and oxygen in charcoal decreases during activation, the proportion of carbon increasing. See also Chapter I, pages 3, 9, and 10, and Chapter IV, pages 120 and 121.

² The best charcoal prepared from purified acetylene contained 0.05 per cent mineral ash (*Private communication* from Professor J. E. Day).

³ H. H. Lowry, *J. Am. Chem. Soc.*, 1924, **46**, 824; *J. Phys. Chem.*, 1929, **33**, 1332; *J. Phys. Chem.*, 1930, **34**, 63.

⁴ H. Violette (*Compt. rend.*, 1853, **36**, 850) showed that charcoal (not activated) was more pyrophoric the lower the temperature of carbonization. The lighter woods have more tendency thereto than the heavier ones. He gives the following table of temperatures of carbonization and the resulting temperatures of spontaneous ignition:

Carbonized at	260°-280°	300°	432°	1,000°-1,500°	1,751°
Ignites at	300°-360°	360°-380°	400°	600°- 800°	1,250°

For a recent attempt at relating temperature of ignition of activated

Deisenhammer¹ considers that cellulose is dissolved in the zinc chloride activation, explaining the fine pulverization, and that the double bonds and carboxyl groups determine the acidic character and the fact that zinc chloride charcoal cannot be regenerated after use. They resemble humic acids. Sorption here may therefore be largely chemical in nature. Alexander² points out how adhesion comes into evidence when local overheating causes carbonaceous materials to "burn" on to stills, flasks, cook-pots or the cylinders of motor cars. When it is highly carbonized, it becomes difficult to remove completely by mechanical means. "It seems as if the nascent bonds, appearing as the more or less profound chemical changes occur, tend to be satisfied by whatever is nearest."

Bangham and Stafford³ induced graphite to take up large quantities of hydrogen under the influence of the electric discharge. Thereupon it became a good sorbent for oxygen. They suggest direct chemical union of the hydrogen, and then of the oxygen, with the carbon, whose mutually saturated bonds had been changed to bonds of ethylenic type. A similar view as to the creation of unsaturated bonds is taken by Lowry⁴ and especially supported by the data of Lowry and Morgan which show that the excessively finely divided graphite prepared by the explosion of graphitic acid shows a sorptive capacity $\frac{1}{3}$ to $\frac{1}{4}$ of that of the best active charcoal.

charcoals to various factors, see M. Świderek *Roczniki Chem.*, 1930, **10**, 365; W. Świentoslawski and M. Chorazy, *Przemysł Chem.*, 1928, **12**, 31; W. Świentoslawski and B. Roga, *Przemysł Chem.*, 1928, **12**, 38; F. Krczil, *Untersuchung und Bewertung technischer Adsorptionsstoffe*, p. 130.

¹ E. Deisenhammer, *Centr. Zuckerind.*, 1926, **34**, 641, 1024.

² J. Alexander and J. W. McBain, Alexander's *Colloid Chemistry*, Vol. III. Chemical Catalogue Co., Inc., New York, 1931.

³ D. H. Bangham and J. Stafford, *J. Chem. Soc.*, 1925, **127**, 1085.

⁴ H. H. Lowry and S. O. Morgan, *J. Phys. Chem.*, 1925, **29**, 1105; H. H. Lowry and R. M. Bozorth, *J. Phys. Chem.*, 1928, **32**, 1524; H. H. Lowry, *J. Phys. Chem.*, 1930, **34**, 63. See R. M. Burns and G. A. Hulett, *J. Am. Chem. Soc.*, 1923, **45**, 572.

Herbst¹ explains his findings that charcoal or carbonized cotton wool sorb at least a thousand times more carbon dioxide than cotton wool, dry wood, paraffin or pulverized sugar as showing that the charcoal exposes free unsaturated valencies of carbon.

Ruff, Rimrott and Zeumer² find that chlorine and bromine combine so firmly with tar-free wood charcoal that evacuation for one hour at 600°–800° C. did not remove any considerable amount and that even boiling with a 10 per cent solution of sodium hydroxide for one hour was ineffective. With ammonia and water, carbon dioxide and hydrogen cyanide are formed.

Wibaut³ finds that sulphur introduced into sugar charcoal by heating at 1,000° cannot be extracted with toluene by heating in a current of nitrogen or in vacuo and only partially by prolonged shaking with bromine water or by heating for five hours at 750° in a current of hydrogen.

In air and steam activation much of the original structure of the charcoal is retained. Often the original wood can be identified by microscopic examination. Lamb, Wilson and Chaney⁴ publish photographs of charcoal before and after such activation, which show that the compact substance of the charcoal between the coarser channels develops a finely granular appearance just visible under the highest powers of the microscope and constituting what they term the "grosser porous structure on which the adsorption really depends". Activated charcoal of this type is regenerable after use by a repetition of the activating process. Dyes sorbed from solution may likewise be removed by alkaline solutions.

¹ H. Herbst, *Biochem. Z.*, 1921, **115**, 204; *Dissert.*, Berlin, 1920. See also O. Ruff, *Kolloid-Z.*, 1926, **38**, 174.

² O. Ruff, E. Rimrott and H. Zeumer, *Kolloid-Z.*, 1925, **37**, 270.

³ J. P. Wibaut, *Proc. Acad. Sci.*, Amsterdam, 1921, **24**, 114; *Verslag. Akad. Wetenschappen*, Amsterdam, 1922, **30**, 86.

⁴ A. B. Lamb, R. E. Wilson and N. K. Chaney, *J. Ind. Eng. Chem.*, 1919, **11**, 429. See also M. E. Barker, *Ind. Eng. Chem.*, 1930, **22**, 929. See also the clearly cellular structure in the photograph by W. E. Garner and F. E. T. Kingman, *Trans. Farad. Soc.*, 1929, **25**, 28.

Such charcoal would appear to consist largely of the skeletons of cellulose micelles and molecules, and the persorption (page 64) may well be due to primary and secondary valencies such as accompany cyclic double bonds.¹

The effect of activation on the sorptive power of wood charcoal is illustrated in table 6 by some figures of Ruff² for alderwood and other charcoals in which the original is compared with that after activation (the isotherms for activated and original charcoals were similar in form).

TABLE 6

The Effect of Activation on the Sorptive Power of various Charcoals

Charcoal		1 g. sorbs c.c. of gas at 0° C. and 700 mm. Hg.			100 g. sorbs grams Phenol from 1 per cent solution
		Argon	CO ₂	NH ₃	
Alderwood	original	2.85	16.5	38.8	< 0.4
"	activated	11	66.2	149	18.9
Coconut	original	10.26	44.5	125	< 1
"	activated	15.96	76.7	208	15.5
Soot from C ₂ H ₂	original	1.59	8.1	18.75	2.5
"	activated	6.25	37.5	109	19
Supra-Norit	original	10	55	—	< 1
"	activated	12.75	81	274	50
" Carbon IV "		10.25	59	150	23.4

Lamb, Wilson and Chaney³ adduce the following data (table 7) for various charcoals, activated in the laboratory, from which the relative values may be appraised. The service time is that which elapsed under standard conditions until the chloropicrin could be detected in the effluent air.

¹ E. Deisenhammer, *Centr. Zuckerind.*, 1926, **34**, 641, 1024.

² O. Ruff, *Z. angew. Chem.*, 1925, **38**, 1164; O. Ruff and G. Roesner, *Ber.*, 1927, **60**, 414. M. E. Barker (*Ind. Eng. Chem.*, 1930, **22**, 926) showed that upon activation there may be a hundred-fold increase in the amount of carbon tetrachloride taken up from the saturated vapour per gram of solid.

³ A. B. Lamb, R. E. Wilson and N. K. Chaney, *J. Ind. Eng. Chem.*, 1919, **11**, 430.

TABLE 7
Comparison of Activated Charcoals from Various Sources.

Base Material.	Bulk Primary Charcoal.	Density Activated Charcoal.	Steam Treatment at 900°.		Accelerated Chloropicrin Test Results.	
			Time Min.	Weight Loss Per cent.	Weight Absorbed Per cent.	Service Time Min.
Sycamore . . .	0.158	0.080	18	53	41	7.3
Cedar . . .	0.223	0.097	60	88	78	16.0
Mountain mahogany . .	0.420	0.236	60	44	32	16.3
Ironwood . .	0.465	0.331	60	44	31	20.8
Brazil nut . .	0.520	0.316	120	71	46	32.2
Ivory nut . .	0.700	0.460	120	70	48	47.0
Cohune nut . .	0.659	0.502	120	48	51	53.4
Babassu nut .	0.540	0.322	210	68	85	58.7
Coconut . . .	0.710	0.445	120	60	61	58.4
Coconut . . .	0.710	0.417	180	75	72	64.4
<i>Briquetted Materials.</i>						
Sawdust . . .	0.542	0.365	120	66	53	40.0
Carbon black .	0.769	0.444	240	64.3	53	50.5
Bituminous coal	0.789	0.430	165	61	58.3	46.8
Anthracite coal	0.830	0.371	480	81	53	40.7

Ray¹ adduces an interesting study of 20 g. of coconut shell charcoal steam activated at 1,000° C., the activation being continued until about 60 per cent of the charcoal was oxidized. The results are shown graphically in fig. 24. The "saturation" values were obtained by drying and evacuating samples and then saturating them with the vapour of carbon tetrachloride. The "retentivity" is the amount retained when the saturated carbon was heated at 100° and the pressure reduced to 2 mm. During the loss of the first 20 per cent of the weight of the charcoal, the material removed had an average percentage hydrogen content of 11.6 and was evidently hydrocarbon. Thereafter the material removed had an average percentage hydrogen content of only 0.78.

¹ A. B. Ray, *Chem. Met. Eng.*, 1923, **28**, 981.

Philip, Dunnill and Workman,¹ and also Page,² have made systematic studies of air activation. They found that powdered charcoals heated in an atmosphere of nitrogen for 24 hours at 800° lost greatly in weight, evolving carbon

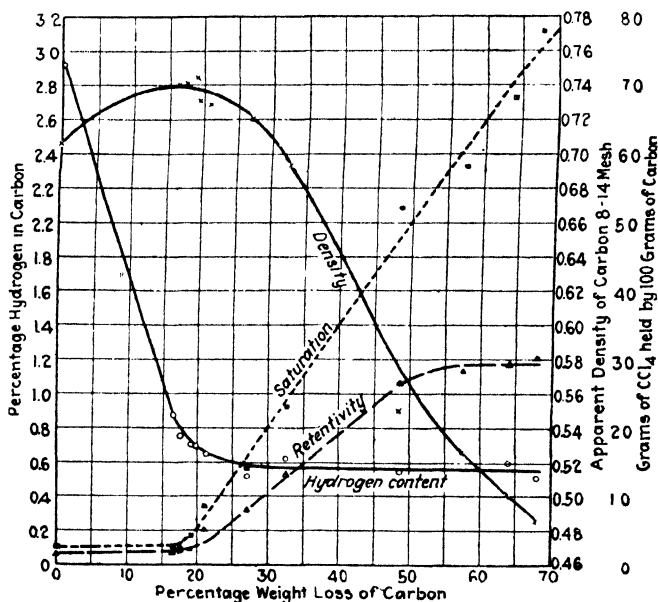


Fig. 24.—Variations in properties of Coconut Charcoals steam activated for various lengths of time at 1,000° C.

dioxide and carbon monoxide. Their observations are given in table 8.

TABLE 8
The Effect of Air Activation on various Charcoals

Charcoal.	Loss of weight, per cent	Bulk density		Percentage of methylene-blue removed from solution.	
		Before	After	Before	After
Japanese ash . . .	34	0.52	0.41	13.0	38.7
Birch	27	0.62	0.48	2.5	16.0
Animal	46	0.41	0.29	17.4	36.4

¹ J. C. Philip, S. Dunnill and O. Workman, *J. Chem. Soc.*, 1920, **117**, 362.

² A. B. P. Page, *J. Chem. Soc.*, **1927**, 1476.

They observed much greater activation when various portions of oxygen were admitted with the nitrogen. The temperature had to be above 800° . The increase in sorptive power paralleled the decrease in bulk density of the powdered activated charcoal. Bulk density is estimated by the size of the container required for a given weight of powder. With some active charcoals the weight of a litre of the powder may be as low as 30 gms. Page's ¹ data are of interest in that they refer to 80 samples prepared under different conditions from the same birchwood. The most important single factor was the total amount of oxygen admitted during oxidation.

For methods of analysis and characterization of various sorbing agents including charcoal, reference may be made to Krczil.²

Honig³ has carried out a very thorough comparison of the chemical compositions and of the reactions with various reagents and of the sorptive capacities towards various solutions of five charcoals, including blood charcoal and a pine-wood charcoal formed at 700°C. , which were not activated. The latter was activated with steam to produce a charcoal of the type of Norit and with steam and flue gases to produce one of the type of Supra-Norit. Finally, another portion of the pinewood was impregnated with zinc chloride and carbonized at 500° to imitate Carboraffin. Since he did not measure the sorption of gases, comparative data for sorption from solutions are given in table 9, which shows the number of milli-

¹ A. B. P. Page, *J. Chem. Soc.*, **1927**, 1476.

² F. Krczil, *Untersuchung und Bewertung technischer Adsorptionsstoffe*, pp. 4-134.

³ P. Honig, *Kolloidchem. Beihefte*, 1926, **22**, 345. For analyses of animal charcoals after various treatments see R. F. Smith, *Chem. News*, 1876, **33**, 100; O. Ruff and E. Hohlfeld, *Kolloid-Z.*, 1924, **34**, 135; O. Ruff, S. Mugdan, E. Hohlfeld and F. Feige, *Kolloid-Z.*, 1923, **32**, 225. Z. Vytopil (*Z. Zuckerind. czechoslovak. Rep.*, 1927, **52**, 63) classifies five different activated charcoals according to colour, macro- and microscopic appearance, decolorizing power, moisture, ash content, ash colour, and ash reaction, carbon content, weight per litre and specific gravity by pycnometer and alcohol.

grams of solute sorbed per gram of charcoal where the concentration is 5 millimols per litre.

TABLE 9

Comparison of Sorptive Capacities of five Charcoals towards various Solutions

	Iodine	Acetic acid	Phenol	Quinine	Methylene blue
Blood charcoal . . .	5.6	0.44	1.85	0.63	1.59
Pine charcoal . . .	0.3	0.27	---	---	0.025
" Norit " . . .	6.2	0.35	1.7	0.49	0.50
" Supra-Norit " . . .	6.9	0.47	2.5	0.69	2.00
" Carboraffin " . . .	4.3	0.54	1.75	0.56	1.26

These charcoals are not carbon, as is emphatically shown in table 10.

TABLE 10

Chemical Composition of five different Charcoals in per cent by Weight

	Blood charcoal	Pine charcoal	" Norit "	" Supra-Norit "	" Carbor-affin "
Water . . .	15.40	6.30	10.20	12.60	17.20
C (on dry wt.) . . .	82.97	88.10	95.30	97.60	85.90
Ash (" ") . . .	8.02	0.32	2.20	0.38	3.30
H ₂ (" ") . . .	0.95	2.8	1.6	0.8	2.2
N ₂ (" ") . . .	3.12	0.50	0.29	0.40	0.39
S (" ") . . .	0.69	0.38	0.34	0.09	0.44
O ₂ (on ash free) . . .	4.95	7.92	0.30	0.72	8.07

Honig also found that prolonged activation with steam increases the carbon content of the charcoal, the specific gravity, the adsorptive power and the heat of wetting.

Kahlbaum's "active charcoal" contains, according to Hene,¹ 74.15% C, 3.26% N₂, 0.63% H₂, 3.00% ash, 19.36% moisture and no sulphur.

Ogawa² determined the composition of various charcoals

¹ W. Hene, *Dissert.*, Hamburg, 1927, p. 11.

² I. Ogawa, *Biochem. Z.*, 1926, **172**, 249. Also detailed analyses of British and American charcoals, extracts and sublimes have been made by P. G. T. Hand and D. O. Shiels, *J. Phys. Chem.*, 1928, **32**, 452.

before and after activation by heating, with the results shown in table II.

TABLE II

Composition of Charcoals before and after Activation by Heating

Source of charcoal	Normal composition			After activation		
	% C.	% O.	% H.	% C.	% O.	% H.
Sugar . .	95.2-95.3	4.0-4.1	0.1	95.4-95.5	4.1	0.5
Naphthalene	90.9-90.7	7.8-7.9	1.3-1.4	91.8	7.4	0.8
Paraffin .	89.7-90	8.8-9.2	1.1-1.2	90	8.9	1.1

All authorities agree that the densest original materials, when fully activated, have the highest sorptive capacity, at least for gases of low molecular weight. This is evidently because of the ultramicroscopic or molecular dimensions of the significant "pores" or interstices. Chaney, Ray and St. John¹ state that the optimum bulk density of gas sorbing charcoals is 0.4 (for 8-10 mesh granules). Hence 1 gm., whilst apparently taking up a volume equal to 2.5 c.c., would really occupy only 0.5 c.c., or 80 per cent of the total would be interstices between carbon atoms and chains (they estimate 66 per cent for a single granule).

Analyses of thirteen other different sorts of active charcoals are given by Kausch.² Patterson describes careful chemical examination of charcoals and their constituents.³

Another very interesting comparison of the sorption of gases by seven different materials has been published by Briggs,⁴ whose approximate data are reproduced in table 12. The volumes of gas are calculated to cubic centimetres at normal temperature and pressure. To them should be added

¹ N. K. Chaney, A. B. Ray and A. St. John, *Ind. Eng. Chem.*, 1923, **15**, 1245.

² O. Kausch, *Die Aktive Kohle*, p. 18.

³ T. L. Patterson, *J. Soc. Chem. Ind.*, 1903, **22**, 608; see also C. R. Johnson, *Ind. Eng. Chem.*, 1928, **20**, 904; M. E. Barker, *Ind. Eng. Chem.*, 1930, **22**, 927.

⁴ H. Briggs, *Proc. Roy. Soc. (London)*, A, 1921, **100**, 88. It may be mentioned here that A. Piutti (*Rend. accad. sci. Napoli*, 1922, **28**, 91; *Giorn. chim. ind. applicata*, 1923, **5**, 70) found by a dynamic method that oak charcoal, dry hemoglobin and walnut charcoal dried after soaking in ammonia sorbed 5.9, 6.0 and 30 volumes of carbon monoxide, respectively.

about 5.5 c.c. for each cubic centimetre of gross volume of carbon or silica, representing the nitrogen liberated on heating from 18° to 300°.

TABLE 12

Sorption of Nitrogen and Hydrogen at Liquid Air Temperature and Atmospheric Pressure

Substance.	Dry Nitrogen.		Dry Hydrogen.		Ratio. Hyd./Nitr.
	C.cs. at N.T.P. sorbed per c.c. (gross volume) of substance.	C.cs. at N.T.P. sorbed per gram of substance.	C.cs. at N.T.P. sorbed per c.c. (gross volume) of substance.	C.cs. at N.T.P. sorbed per gram of substance.	
Coconut charcoal (activated by steaming)	129	247	66.3	127	0.60
Plum stone charcoal (activated) . . .	91.2	—	56.7	—	0.72
Birch charcoal (activated)	44.5	202	27.0	123	0.62
German impregnated charcoal 1918 . .	121	303	25.5	63.8	0.28
Blood charcoal . .	91.1	—	36.3	—	0.40
Sutcliffe-Speakman's preparation of briquetted coal, charcoal and dusts .	91.8	206	43.1	96.7	0.47
Cleveland (U.S.A.) activated anthracite	84.9	89.7	53.1	56.3	0.63
Graphite ground . .	5.6	—	2.7	—	0.49
Colloidal silica (Briggs)	203	376	26.7	51.6	0.12
Dried silica gel (Baltimore, U.S.A.) . .	115	142	—	—	—

" DENSITY " OF CHARCOAL ¹

There are four kinds of density of charcoal which have to be distinguished: bulk density, which is the weight of charcoal per unit of volume of a containing vessel; apparent density, determined by displacement of mercury which cannot

¹ For a discussion of this subject with practical details, see F. Krczil, *Untersuchung und Bewertung technischer Adsorptionsstoffe*, 1931, pp. 71-III.

enter microscopic and ultramicroscopic pores ; specific gravity (often called real density) ¹ as determined by displacement of penetrating or partially penetrating liquids such as water ; and lastly, true density of the close-packed, solid material of which the charcoal is composed.

These densities correspond to three kinds of interstices or voids : first, spaces between granules and particles or powders, and coarse channels ; second, microscopic pores and channels and interstices of colloidal dimensions ; third, spacings of fine ultramicroscopic, molecular or atomic dimensions, such as are lacking in close-packed, continuous space lattices or in a liquid. The " true density " remains as that which corresponds to a close-packed space lattice, such as diamond or graphite, or the close-packing of molecules which in practice we assume in liquids. We assume this because of the extremely slight compressibility of liquids and crystals. If matter were really continuous, that is, not molecular and atomic in structure, it would be much easier to define " pores " of all sizes ranging from the spaces between large lumps of coal down to those indefinitely small. However, matter is not a continuum and protons, electrons, atoms and molecules are not of accurately defined size. If molecules are of definite shape, they cannot be in complete contact with contiguous molecules, even in liquids. This is borne out by X-ray examination of liquids.² Strict definition is therefore difficult, the more so because the space lattices of many substances are sufficiently open to permit the free passage of foreign molecules (see, for example, Chapter V dealing with chabasite). However, we shall consider that the space lattice of a crystal of graphite affords no such possibility, because the successive layers comprising the crystal are " in direct contact ".

It is far otherwise with charcoal. Its formation, often from highly porous, elaborate living structures, through disruptive evolution of gases from all its parts, and the wasting and gasification of portions of the carbon structure itself,

¹ Chaney, etc.

² See, for example, C. M. Sogani, *Indian J. Phys.*, 1927, **2**, 113 ; J. W. McBain, *J. Chem. Educ.*, 1929, **6**, 2115.

leaves a conglomerate of skeletons of cells and micelles and space lattices, a large part of which is permeable by such minute particles as helium atoms.

Many investigators have been led to this general picture of the structure of charcoal, for the finest discontinuities are too small to admit colloidal particles and the larger molecules but are still accessible to small molecules. We shall adopt for it the term "ultraporosity". This term (which corresponds to the "molecular roughness" or "molecular roughening up" of Magnus¹ or the "atomic gaps" of Ruff²) was introduced by Herbst,³ although upon wholly inadequate experimental grounds. He used it as an explanation of why sulphur dioxide was sometimes sorbed to a less extent than carbon dioxide, assuming that sulphur dioxide was representative of large molecules and taking carbon dioxide as his standard of reference as a small molecule; whereas there is in fact little or no difference in the size of these two molecules,⁴ and under comparable conditions sulphur dioxide was sorbed to a far greater extent than carbon dioxide. As we shall see in Chapter V, a crystal of chabasite constitutes a perfect example of a molecular sieve.

The X-ray study of diamond, graphite and typical organic crystals, both aliphatic and aromatic, throws considerable light upon the minimum dimensions with which we have to deal within a piece of charcoal. Carbon atoms, which are bound by primary valencies in organic compounds or in diamond, have a distance from centre to centre of 1.5 Å. The distance of closest approach of carbon atoms belonging to different molecules is, however, only about 3.5 Å. This is the distance apart of consecutive molecules in naphthalene and in fatty acids.⁵ The layers in graphite are separated by

¹ A. Magnus, *Z. anorg. allgem. Chem.*, 1926, **155**, 220.

² O. Ruff and G. Roesner, *Ber.*, 1927, **60**, 415.

³ H. Herbst, *Biochem. Z.*, 1921, **115**, 204; *Dissert.*, Berlin, 1920.

⁴ *International Critical Tables*, 1929, **5**, 3, 4; A. O. Rankine and C. J. Smith, *Proc. Phys. Soc. (London)*, 1923, **35**, Pt. 1, 33; A. O. Rankine, *Proc. Roy. Soc. (London)*, A, 1921, **98**, 369.

⁵ For a table of similar distances, see S. B. Hendricks, *Chem. Reviews*, 1930, **7**, 441, 474.

a distance of 3.41 Å. The glucose chains which make up the monoclinic micelles of cellulose are in planes 3.95 Å. apart. It is obvious that we can give an approximate determination of different kinds of bindings in terms of these distances. It is evident that chemisorption of, for example, oxygen, where carbon and oxygen atoms are even closer than primarily linked carbon atoms, can occur in regions to which persorption of oxygen or nitrogen molecules could not extend.

Mere magnitude of molecular size is not the sole determining factor in penetration and persorption, even when this is of the purely physical type. Specific attraction plays a definite rôle. Suitable molecules may enter openings originally too small for them as is evidenced by the distention of the charcoal which accompanies persorption. This topic is further discussed in Chapter XIII. Spacings between the centres of adjacent atoms corresponding to various types of chemical bonds have been compiled by Latimer,¹ the values being assembled in table 13. Later studies of the Raman effect

TABLE 13

*Spacings between the Centres of adjacent Atoms corresponding to various Types of Chemical Bonds*²

Bond	Dist. bet. atomic centres, Å.	Bond	Dist. bet. atomic centres, Å.	Bond	Dist. bet. atomic centres, Å.
C—H . . .	1.20	C—Cl . . .	1.70	N—S . . .	1.65
C—C . . .	1.52	C—Br . . .	1.85	N—Cl . . .	1.64
C=C . . .	1.47	N—H . . .	1.15	N—Br . . .	1.79
C—N . . .	1.46	N—N . . .	1.40	O—H . . .	1.05
C=N . . .	1.20	N=N . . .	1.21	O—O . . .	1.30
C—O . . .	1.41	N—O . . .	1.35	O=S . . .	1.56
C=O . . .	1.29	N=O . . .	1.20	O—Cl . . .	1.52
C—S . . .	1.71				

¹ W. M. Latimer, *J. Am. Chem. Soc.*, 1929, **51**, 3186; P. Debye, L. Bewilogua and F. Ehrhardt (*Ber. Verhandl. sächs. Akad. Wiss. Leipzig*, 1929, **81**, 29) deduce from X-ray scattering the distance between chlorine atoms as 3.1 Å. for CCl₄, 3.4 for CHCl₃ and 3.9 for CH₂Cl₂.

² For later tables see S. B. Hendricks, *Chem. Reviews*, 1930, **7**, 441, 473; also dimensions of space lattices of organic molecules.

and band spectra give values some of which agree with those in the table whilst others are distinctly different.

In an interesting scale diagram of oxygen molecules adsorbed upon a plane surface, Polányi¹ places the atomic centres 0.8 Å. apart for atoms of the same molecule, but a minimum of 3 Å. apart for oxygen atoms of two adjacent molecules.

Titani² lists the diameters of the molecules of sixteen simple organic substances in addition to those of sulphur dioxide and air. The former range from 3.33 Å. for acetylene to 4.79 Å. for iso-amylene, the latter being 3.53 Å. and 3.11 Å., respectively.

The various densities of charcoal range from 0.03 to about 1 for bulk density; 0.3 to 1.3 for apparent density; 1.2 to 2.1 for specific gravity; and up to 2.2 or 2.3 for the true density of the solid material. The density of diamond is 3.47 to 3.56; that of graphite is 2.25 to 2.26.

Weight for weight the sorptive powers of various charcoals from shells and woods do not differ greatly, and therefore are roughly in proportion to the respective bulk densities,³ as, for example, with charcoal from the shell and edible portion of the coconut.⁴

The apparent density of charcoal (in mercury) has been

¹ M. Polányi, *Z. Elektrochem.*, 1929, **35**, 563.

² T. Titani, *Bull. Chem. Soc. Japan*, 1930, **5**, 98.

³ See for example, J. Sameshima and K. Hayashi, *Sci. Repts. Tōhoku Imp. Univ.*, 1924, **12**, 289, where sorption capacities for air at low temperatures are compared. J. Sameshima (*Bull. Chem. Soc. Japan*, 1927, **2**, 1) found that at room temperature and one atmosphere pressure the volume of carbon dioxide (at N.T.P.) sorbed by one gram of charcoal ranged between 37 and 54 c.c. for the following sources: bamboo, cherry and ebony wood, cork, rice, coconut shell, cane sugar, naphthalene, soot, anthracite and Kahlbaum's "Kohle aktiv", cane sugar giving the highest result.

⁴ For example, J. B. Firth, *Trans. Farad. Soc.*, 1920, **16**, 434. J. Dewar (*Proc. Roy. Inst. Gr. Brit.*, 1905, **18**, 180) found that at the temperature of liquid air coconut charcoal and sugar charcoal sorb the same amounts of hydrogen.

measured by many workers.¹ Some examples are given in table 14.²

TABLE 14³

The apparent Density of various Woods and the corresponding Charcoals (in Mercury)

Kind of wood	Apparent specific density of the air-dried wood (Hg)	Apparent density of charcoal (Hg)
Linden . . .	0.35-0.6	0.4
Poplar . . .	0.4 -0.6	0.4 -0.5
Red fir . . .	0.35-0.6	0.4 -0.52
Scotch pine . . .	0.31-0.76	0.39-0.55
White fir . . .	0.37-0.75	0.4 -0.55
Maple . . .	0.53-0.8	0.5 -0.6
Elm . . .	0.53-0.82	0.5 -0.6
Acacia . . .	0.58-0.85	0.5 -0.6
Walnut . . .	0.6 -0.8	0.6 -0.7
Hornbeam . . .	0.6 -0.82	0.67
Red beech . . .	0.66-0.83	0.6 -0.7
Oak . . .	0.7 -1.0	0.7 -0.8
Holmoak . . .	0.7 -1.05	0.85

The specific gravities of various wood charcoals as measured in water are given in table 15.⁴ The values in the second

¹ T. de Saussure (*Gilbert's Ann. der Physik*, 1814, **47**, 113; *Ann. Phil.*, 1815, **6**, 241, 331) found that powdered charcoals from different materials possess only imperceptible sorption if the apparent density is too small or too great, as for example, with that from cork (0.1) and Cumberland black lead (2.18), the latter being 96 per cent carbon. Fir, boxwood and Russiberg coal with apparent densities 0.1, 0.6, 1.3 sorbed 4.5, 7.5 and 10.5 times their own volume of air, respectively.

² H. Herbst, *Kolloidchem. Beihefte*, 1925, **21**, 35. M. E. Barker (*Ind. Eng. Chem.*, 1930, **22**, 926) gives the apparent (granule) density of primary coconut charcoal as 0.96 before activation and as 0.84 when excellently activated. Other values for iron wood and lignite are also given.

³ H. Violette (*Compt. rend.*, 1853, **36**, 850; *L'Institut*, 18 Mai, 1853; *Ann. chim. phys.*, (3), 1853, **39**, 291) points out that all kinds of woods and even cork, if finely powdered, give the same specific gravity in water; namely, 1.520. He finds that the charcoal exhibits a density depending upon the temperature of carbonization, being 1.507 for 150°, 1.402 for 270°, 1.500 for 350°, and rises to 2.002 for charcoal carbonized at 1,500°. Compare the table on page 68 for activated charcoal.

⁴ A. Piutti and G. Magli, *Gazz. chim. ital.*, 1910, **40**, I, 569.

column are the cubic centimetres of gas evolved per bulk cubic centimetre of charcoal on heating from -190° to 550° .

TABLE 15¹

The Specific Gravities of various Wood Charcoals as measured in Water

Charcoal	Gas evolved per c.c.	Specific gravity (H ₂ O)
Prunus cerasus (<i>kernels</i>) (Japanese cherry)	280.1	1.6393
Cocos nucifera (<i>shell</i>) (Coco palm)	251.8	1.4497
Phillyrea media (<i>branches</i>) (Mock privet)	222.4	1.4970
Grevillea robusta (<i>branches</i>) (Silk oak)	212.7	1.4383
Abies alba (<i>trunk</i>) (Fir)	199.5	1.1901
Castanea vesca (<i>trunk</i>) (Common chestnut)	186.3	1.3000
Buxus sempervirens (<i>trunk</i>) (Common boxwood)	138.5	1.4192
Diospyros kaki (<i>branches</i>) (Japanese persimmon)	134.5	1.3398
Populus nigra (<i>trunk</i>) (Lombardy poplar)	134.1	1.2802
Prunus virginiana (<i>branches</i>) (Choke cherry)	133	1.2359
Ceratonia siliqua (<i>seeds</i>) (St. John's bread)	131.5	1.6274
Prunus armeniaca (<i>kernels</i>)	129.5	1.3994
Juglans regia (<i>trunk</i>) (English walnut)	118.6	1.3132
Pinus rigida (<i>trunk</i>) (Pine)	111.1	1.3114
Robinia pseudoacacia (<i>branches</i>) (Black locust)	99.9	1.2218
Buxus sempervirens (<i>twigs</i>) (Common boxwood)	92.4	1.1748

¹ Much more comprehensive measurements of the air sorbed by charcoal at various temperatures between -185°C. and room temperature by many different typical charcoals together with observations of bulk densities have been made by K. Hayashi (*J. Chem. Soc. Japan*, 1922, **43**, 535), some results being quoted in full in *Chemical Abstracts*, 1923, **17**, 11; as well as by J. Sameshima and K. Hayashi (*Sci. Reports Tôhoku Imp. Univ.*, 1924, **12**, 289). A. D. Monroe (*J. Soc. Chem. Ind.*, 1922, **41**, 129T) has similarly investigated the gases evolved from a series of different coals upon evacuation, noting the relative amounts of oxygen, nitrogen, carbon dioxide and methane evolved and readsorbed.

Other determinations of specific gravities of various charcoals as measured in water are as follows: blood, 1.96;¹ coconut shell, 1.92,² 1.904,³ 1.88 (steam activated),⁴ 1.86,⁵ 1.85 (active),⁶ 1.74 (raw),⁴ 1.67;⁷ coconut (edible portion), 1.85;² sugar, 1.786;³ elder pulp, 1.78;² linden wood, 1.74;² Aussig A-Kohle, 1.637;⁸ primary ironwood, 1.46;⁶ active ironwood, 1.86;⁶ low temperature lignite coke, 1.43.⁶ Lowry and Hulett⁹ give the following values for specific gravities, (in water) and bulk densities of heated and evacuated, activated, gas-mask charcoals:—

	"A 909"	Nela	English birch	German ¹⁰
	(steam)	(steam)	(air)	(ZnCl ₂)
Specific gravity . . .	1.84	1.89	1.86	1.70
Bulk density . . .	0.55	0.46	0.13	0.24

Pickles¹¹ obtained the following values for specific gravities (in water) and bulk densities of charcoals which had been previously heated to expel air:

Charcoal	Almond	Birch chips	Fruit stone	Birch dust	Coco- nut	Palm nut
Specific gravity . . .	1.70	1.44	1.72	1.47	1.71	1.59
Bulk density . . .	0.48	0.23	0.68	0.21	0.63	0.64

Ward and Rideal¹² obtained somewhat different values from those already cited; namely,

¹ A. M. Williams, *Proc. Roy. Soc. (London)*, A, 1920, **98**, 223; compare A. Reyckler, *Gedenkboek van Bemmelen*, 1910, p. 58.

² H. Baerwald, *Ann. der Physik*, (4), 1907, **23**, 87.

³ J. B. Firth, *Trans. Farad. Soc.*, 1923, **19**, 444.

⁴ H. Briggs, *Proc. Roy. Soc. (London)*, A, 1921, **100**, 92.

⁵ A. Titoff, *Z. physik. Chem.*, 1910, **74**, 646.

⁶ M. E. Barker, *Ind. Eng. Chem.*, 1930, **22**, 930.

⁷ I. F. Homfray, *Z. physik. Chem.*, 1910, **74**, 152.

⁸ F. Goldmann and M. Polányi, *Z. physik. Chem.*, 1928, **132**, 321.

⁹ H. H. Lowry and G. A. Hulett, *J. Am. Chem. Soc.*, 1920, **42**, 1394.

¹⁰ E. Berl and K. Andress (*Z. angew. Chem.*, 1921, **34**, 369) give for a similar charcoal bulk density 0.286, apparent density (in Hg) 0.674, and specific gravity (liquid not mentioned) 1.83.

¹¹ A. Pickles, *Chem. News*, 1920, **121**, 1. See also P. G. T. Hand and D. O. Shiels, *J. Phys. Chem.*, 1928, **32**, 455.

¹² A. F. H. Ward and E. K. Rideal, *J. Chem. Soc.*, **1927**, 3119.

Charcoal	Specific gravity (water)	Bulk density
Merck's blood	1.37	0.22
Sugar	1.42	0.58
Activated sugar	1.43	0.30
Supra-Norit	2.03	0.14

Specific gravities measured in other liquids are collected in table 16 on page 88 in which each vertical column refers to a single specimen of charcoal.

The specific gravity of charcoal as determined with wetting liquids depends remarkably upon the liquid employed (see table 16). It is always distinctly less than the density of graphite and opinions differ radically as to the explanation of this behaviour. One school represented by Williams,¹ Briggs,² Harkins³ and Polányi⁴ interprets such data as indicating that the true density of the solid material of the charcoal is really far less than that observed, because they assume that the liquid in the neighbourhood of the charcoal is highly compressed and therefore adds a fictitious amount to the density of the charcoal. Thus Briggs estimated the true density of charcoal at 1.33, Williams and Polányi placed it at 1.45 or 1.5, and Harkins and Ewing concluded that it was 1.6. Williams' argument was that since chloroform gave 2.17 and water 1.96, 11,000 atmospheres would be required to equalize the volumes of water and chloroform on this basis, and, therefore, allowing for their compression, the true volume displaced by the carbon must only be 0.67 c.c. per gram, corresponding to a true density of 1.45 in place of the much higher ones observed. Table 17 was drawn up by Harkins and Ewing⁵ to show the possibility of this interpretation on the basis of parallelism between specific gravity and compressibility of the liquid.

¹ A. M. Williams, *Proc. Roy. Soc. (London)*, A, 1920, **98**, 223.

² H. Briggs, *Proc. Roy. Soc. (London)*, A, 1921, **100**, 88.

³ W. D. Harkins and D. T. Ewing, *J. Am. Chem. Soc.*, 1921, **43**, 1787.

⁴ F. Goldmann and M. Polányi, *Z. physik. Chem.*, 1928, **132**, 321.

⁵ W. D. Harkins and D. T. Ewing, *J. Am. Chem. Soc.*, 1921, **43**, 1790.

TABLE 16

*Specific Gravities of Specimens of Charcoal as Determined with a Series of Liquids **

Liquid.	H. and E.†	Lowry.‡	G. and P.§	C. and H.	Firth.¶		Porter.**
					Coco-nut Shell.	Sugar.	
Carbon tetra-chloride . . .	---	---	1.630 1.662	1.647	---	---	---
Water . . .	1.843	1.745	1.637	1.854	1.904	1.786	---
Ethyl alcohol . . .	---	1.717	---	---	2.001	1.957	---
Chloroform †† . . .	1.992	---	---	---	2.178	2.221	---
Benzene . . .	2.008	1.718	---	1.797	1.958	1.976	1.693
Carbon disulphide . . .	2.057	---	1.746 1.793	1.984	---	---	---
Acetone . . .	2.112	1.739	---	---	---	---	---
Ether . . .	2.12	---	1.797	---	---	---	1.818
Pentane . . .	2.129	---	1.787	---	---	---	---

* N. Goodwin and C. R. Park (*Ind. Eng. Chem.*, 1928, **20**, 622) found that with xylene different carbon blacks range in specific gravity between 1.65 and 1.90.

† W. D. Harkins and D. T. Ewing (*J. Am. Chem. Soc.*, 1921, **43**, 1790) used steam activated coconut shell gas-mask charcoal. They obtained 0.863 as the apparent density of charcoal in mercury.

‡ H. H. Lowry (*J. Am. Chem. Soc.*, 1924, **46**, 824) used 23 different samples of non-activated charcoal prepared from anthracite coal; the specific gravities in water were carefully determined and were between 1.710 and 1.888, the bulk densities being between 0.9 and 1.0. He found 1.723 as the specific gravity of charcoal when immersed in tetrabromo-ethane. Analyses are also given of the content of the charcoals in water, nitrogen, oxygen, carbon dioxide, carbon monoxide and hydrogen.

§ F. Goldmann and M. Polányi (*Z. physik. Chem.*, 1928, **132**, 321) used Aussig A-Kohle (zinc chloride activated) which had been "evacuated" at 500° for five hours. They obtained 1.824 as the specific gravity of charcoal when immersed in ethyl chloride.

|| H. E. Cude and G. A. Hulett (*J. Am. Chem. Soc.*, 1920, **42**, 395) used steam activated coconut shell charcoal which had been evacuated.

¶ J. B. Firth (*Trans. Farad. Soc.*, 1923, **19**, 444) used coconut shell and sugar charcoals which were evacuated but not activated.

** J. L. Porter (1929, unpublished), working in the author's laboratory at Stanford University, used sugar charcoal (Kahlbaum), air activated. He obtained 1.546 as the specific gravity of the charcoal when immersed in heptane.

†† A. M. Williams (*Proc. Roy. Soc. (London)*, A, 1920, **98**, 223) found 2.17 as the specific gravity of purified blood charcoal when immersed in chloroform.

TABLE 17
Comparison, for one Charcoal, of the Specific Gravities measured in different Liquids with the Physical Constants of the Liquids

Liquid	Specific gravity	Surface tension, dynes per cm.	Viscosity in absolute units η	ν	Mol. vol	van der Waals' $a \cdot 10^3$	van der Waals' $b \cdot 10^6$ (mol. size)	Per cent compressibility by 500 atm. at 20°
Water . . .	. 1.843	72.8	0.0101	7.200	18.05	1.185	1.499	2.12
Propyl alcohol . . .	. 1.960	23.7	0.0223	1.062	74.70	3.250	7.577	3.96
Chloroform . . .	. 1.992	27.13	0.0057	4.760	80.17	3.023	4.562	3.94
Benzene . . .	. 2.008	28.88	0.0064	4.510	88.89	3.727	5.369	3.64
<i>p</i> -Xylene . . .	. 2.018	28.33	0.0064	4.430	123.21	6.165	8.077	3.39
Petroleum ether . . .	. 2.042	—	—	—	—	—	—	—
Carbon disulphide . . .	. 2.057	31.38	0.0037	8.480	60.37	2.316	3.431	3.72
Acetone . . .	. 2.112	23.50	0.0033	7.120	73.34	2.774	4.437	4.48
Ether . . .	. 2.120	17.1	0.0024	7.125	103.75	3.496	6.016	6.27
Pentane . . .	. 2.129	about 15	0.0024	6.200	114.25	3.788	6.516	—

The other school, represented especially by Hulett, considers that the true density of the carbon in charcoal is that of graphite, and that the lower specific gravities observed are due to incomplete penetration by the liquids employed. For this there are three kinds of evidence. The first is that of Cude and Hulett¹ who find that the specific gravity increases rapidly after immersion and may require months or even years to obtain a constant value. For example, with the same steam activated coconut charcoal they observed the following specific gravities :

Water	Carbon disulphide	Benzene	Carbon tetrachloride
1.829 (15 min.)	1.915 (15 min.)	1.734 (15 min.)	1.586 (15 min.)
1.854 (119 hrs.)	1.984 (362 hrs.)	1.797 (286 hrs.)	1.647 (2,856 hrs.)

The whole of this change is eliminated and the final density immediately reached if the system is placed under great pressures such as 500 to 9,000 atmospheres.

The second kind of evidence in favour of the view that liquids ordinarily do not completely penetrate is given in table 18 which shows that with increasing activation and porosity the specific gravity increases towards that of graphite.

The most conclusive evidence is that of Howard and Hulett² who have determined the specific gravity, using gaseous helium as the displaced fluid. The sorption of helium by charcoal at room temperature is immeasurably small and its atoms are minute. Table 19 shows very convincingly that the specific gravity of the activated charcoal is likewise its true density and closely approaches that of graphite.

¹ H. E. Cude and G. A. Hulett, *J. Am. Chem. Soc.*, 1920, **42**, 391. See also J. B. Firth, *Trans. Farad. Soc.*, 1923, **19**, 444 ; H. H. Lowry, *J. Am. Chem. Soc.*, 1924, **46**, 833. E. W. Washburn (*Phys. Rev.*, (2), 1921, **17**, 374) found that the rate of penetration was in accordance with the formula for an assemblage of very small capillaries during the initial period but that the ensuing slower rate might be ascribable to the previous complete filling of all except ultrapores.

² H. C. Howard and G. A. Hulett, *J. Phys. Chem.*, 1924, **28**, 1082. S. McLean (*Trans. Roy. Soc. Canada*, (3), 1919, **13**, 197) records far lower values.

TABLE 18 ¹*Sorbing Capacity of Progressively Steam Activated Coconut Charcoals* ²

Sample	Series	Service time (obs.), minutes	Specific gravity (kerosene)	Bulk density
Unactivated	—	0	1.56	0.715
1	D	6	1.66	0.626
2	E	112	1.63	0.634
3	F	250	1.66	0.580
4	D	387	1.87	0.525
13	E	577	2.02	0.497
21	H	687	2.03	0.591
26	F	805	2.11	0.484
29	F	900	2.17	0.452
30	H	955	2.14	0.432

TABLE 19 ³*Specific Gravity of Charcoal (20-40 mesh), using Helium as the Filling Substance*

Sample of charcoal.	Specific gravity	C.c. (at N.T.P.) of N ₂ sorbed by 1 gm. charcoal
Coconut A909 (steam activated) ⁴	2.12	8.8
Pure sugar (vacuum heated at 1,000° C.)	2.26	6.2
Kelp (decolorizing charcoal, about 12 per cent ash)	2.28	5.2
Carbon black (steam activated)	2.05	5.5
Coconut (commercial activated)	2.14	8.2
Willow (ordinary charcoal)	1.44	2.8
Petroleum coke	1.43	0.3
Coke from bituminous coal	1.51	0.5
Ceylon graphite	2.28	None

¹ N. K. Chaney, A. B. Ray and A. St. John, *Ind. Eng. Chem.*, 1923, **15**, 1245; also N. K. Chaney, *Trans. Amer. Electrochem. Soc.*, 1919, **36**, 107; cf. R. M. Winter and H. B. Baker, *J. Chem. Soc.*, 1920, **117**, 319.

² The charcoals are from eight different sources (samples of common source indicated by same series letter between which the degree of oxidation is the only variable).

³ H. C. Howard and G. A. Hulett, *J. Phys. Chem.*, 1924, **28**, 1088. O. Ruff (*Z. angew. Chem.*, 1925, **38**, 1166) found that with tar free charcoal he could get almost as high results with toluene.

⁴ The bulk density was 0.5.

Howard and Hulett¹ draw important conclusions from the data quoted on page 68. Activated charcoal heated to 2,000° acquired the low density of only 1.35 as tested by helium, or less as tested by water. Ordinary charcoal, on the contrary, similarly heated, approaches the density of massive graphite, 2.25 (see, for example, footnote 3, page 84). This shows that the sintered activated charcoal is still essentially discontinuous, although the "pores" or interatomic spaces are now mostly of less than molecular dimensions. This conception is confirmed by their observation that helium requires at least a day to penetrate the charcoal.

From the newer point of view the parallelism in table 17 between specific gravity and the last column is merely another example of the parallelism between sorption and compressibility. In Chapter XVII it is shown that sorbed material may appear to occupy less volume than when free.

Rideal² suggests that part of the incomplete penetration corresponding to the remarkably different specific gravities observed with different liquids is due to previously sorbed material.

Nothing is known of the density of sorbed material. Probably it is close packed, possibly of the same density as the corresponding free liquid, possibly denser. This is being experimentally determined in the author's laboratory.

THE IMPORTANCE OF PRELIMINARY EVACUATION

In view of the foregoing information as to the chemical composition and physical structure of charcoal and the fact that many of the accessible portions are not carbon, it is not surprising to find that the amount and general behaviour of sorption is profoundly modified by the extent to which the charcoal is cleaned by previous heating and evacuation. Seldom or never is the treatment sufficiently drastic to remove all impurity and previously sorbed material. Substances to be sorbed must compete with those already present. For

¹ H. C. Howard and G. A. Hulett, *J. Phys. Chem.*, 1924, **28**, 1082.

² E. K. Rideal, *Trans. Farad. Soc.*, 1926, **22**, No. 71, 437.

example, nitrogen is evolved on mere immersion of charcoal in water.¹

To remove other impurities, prolonged exposure to vacua of the order of 10^{-5} mm. at temperatures approaching 600°C . is not wholly sufficient. This is readily seen from the displacement of impurities when charcoal which has already undergone such treatment is brought into contact with definite vapours whose sorption is to be studied.² The writer strongly

¹ W. Skey, *Chem. News*, 1867, **15**, 15 and 27; G. Craig (*Chem. News*, 1904, **90**, 109), in similar experiments with coke from lignite. Even from solution the sorption is greatly dependent upon the previous treatment of the charcoal. For example, J. B. Firth (*Trans. Farad. Soc.*, 1920, **16**, 434) found that for the sorption of iodine in chloroform the value of x/m with lampblack increased from 0.019 to 0.378 after heating to 120°C ., and to 0.392 after heating in vacuo at 200°C ., whereas in the case of sugar carbon the corresponding values of x/m were 0.367, increasing to 0.387 and 0.393, respectively. C. Heim (*Elektrotech. Z.*, 1886, **7**, 462, 504) found that gas is liberated from a glowing carbon filament in vacuo for many hundreds of hours, the total amounting to a thousand times the volume of the filament. He noted a blue luminescence in the neighbourhood of the filament after high evacuation. R. F. Sessions in the writer's laboratory has observed the same effect in a highly evacuated tube containing carbon heated by induction currents.

² See, for example, R. Chaplin (*Proc. Roy. Soc. (London)*, A, 1928, **121**, 344) who found that carbon tetrachloride displaces gases, including carbon dioxide, from charcoal even after evacuation at 800° at a pressure of 2×10^{-8} mm. Only thereafter did the sorption prove fully reversible. For similar conclusions see S. J. Gregg, *J. Chem. Soc.*, **1927**, 1503. H. S. Harned (*J. Am. Chem. Soc.*, 1920, **42**, 372) found that in no case could reproducible results for rate of sorption be obtained until the charcoal had been heated to more than 700° in a vacuum, cooled in a vacuum, exposed to the gas until a considerable quantity was sorbed and again heated above 700° in a high vacuum. R. F. Sessions points out the further consideration that the washing or soaking of the charcoal in the vapour to be studied must be sufficiently prolonged to enable complete displacement of impurities and foreign gases to take place. See also J. W. McBain, *Nature*, 1926, **117**, 550, and various papers from the author's laboratory. H. Baerwald (*Ann. der Physik*, (4), 1907, **23**, 87) found it impossible to free charcoal from oxygen, nitrogen and hydrogen even at $1,200^{\circ}$. He made a systematic study of the progressive increase in sorption caused by evacuation at temperatures increasing from 20° through 160° , 300° , 400° to 500° .

advises this as a routine procedure followed by a rigorous repetition of the heating and prolonged evacuation.¹ Magnus² would regard this cleaning as an extension of activation, with corresponding increase in the number of pores of molecular dimensions available for sorption.

Improved cleansing of the charcoal by more thorough evacuation not only increases the amount of sorption but greatly alters the form of the curve relating sorption with pressure. The sorption at lower pressures is most affected and therefore the sorption at higher pressures becomes more nearly constant or approaches a saturation value.

The writer quotes experiments from his laboratory which illustrate this increase in sorption.

"For example, carefully prepared sugar charcoal, which had been activated by superficial oxidation at about 1,200°, was given an exposure for five hours at 450° to a vacuum of 10^{-5} mm., and was afterwards found to sorb a maximum of 19.8 per cent of its own weight of nitrous oxide in a protracted series of experiments. The amount of nitrous oxide sorbed was raised to 26.5 per cent by re-evacuating the charcoal at 450° after its saturation with nitrous oxide, and then repeating the measurements. Similar behaviour has been observed in many other cases; for example, the observed sorption of such inert substances as hexane or decane may be increased several fold by repeating the evacuation after the charcoal has been saturated with the hexane or decane to displace other impurities from the surface."³

For contradictory work, see J. B. Firth and F. S. Watson, *Trans. Farad. Soc.*, 1924, **20**, 370; *J. Phys. Chem.*, 1925, **29**, 987. For earlier work (1863) on the spontaneous displacement of nitrogen from charcoal by other gases, see R. A. Smith, *Proc. Roy. Soc. (London)*, A, 1926, **112**, 296. A. J. Allmand and A. Puttick (*Proc. Roy. Soc. (London)*, A, 1930, **130**, 197) consider that the effect of high temperature pre-evacuation is due to the more extensive removal of sorbed oxygen rather than to an increase in surface; they point out that the pressure of carbon tetrachloride has to reach a certain minimum before it efficiently displaces the oxygen.

¹ For an enumeration of factors found to affect sorption, see A. S. Coolidge, *J. Am. Chem. Soc.*, 1924, **46**, 596.

² A. Magnus, *Z. anorg. allgem. Chem.*, 1926, **155**, 220.

³ J. W. McBain, *Nature*, 1926, **117**, 550.

Other illustrations of the striking effect upon the form of the sorption isotherm will be given in the section on the sorption of vapours.

SORPTION OF GASES

Sorption of gases by charcoal may be so large in amount that it approaches chemical proportions, especially in cases of persorption with activated charcoal. One notes, for example, in the experiments of Dewar¹ with ordinary coconut charcoal that the sorbed gas was as much as one atom of oxygen for four atoms of carbon or one atom of hydrogen for seven atoms of carbon.

There are two comprehensive investigations of the sorption of various gases by a single specimen of charcoal from the shell of the coconut, both published in 1910. These data will receive fuller attention, using those of other authors to supplement them. In neither case was adequate care taken to free the charcoal from previously sorbed material.²

Titoff,³ in Freundlich's laboratory, measured the sorption of pure hydrogen, nitrogen, carbon dioxide and ammonia at temperatures from -79°C. to $+151.5^{\circ}\text{C.}$ The charcoal had been heated for 6–8 hours at 550°C. in vacuo, and before use it was heated at 400°C. at 0.001–0.003 mm. His sorption apparatus is shown in Chapter II, page 19, fig. 5.

The values found by Titoff for sorption at two particular pressures—namely, 10 cm. and 70.5 cm. Hg, respectively—at various temperatures are given in table 20 where they are expressed in cubic centimetres at 0° and 760 mm. Hg per gram of charcoal. These results have the advantage that they compare numbers of molecules.

Titoff evaluated all his results by means of the empirical sorption isotherm, $x/m = kp^{1/n}$. The values of $1/n$ for hydrogen were very slightly less than unity; that is, the

¹ J. Dewar, *Proc. Roy. Inst. Gr. Brit.*, 1905, **18**, 183.

² S. Arrhenius (*Medd. Vetenskapsakad. Nobelinst.*, 1911, **2**, No. 7, 28) points out serious numerical discrepancies in their work.

³ A. Titoff, *Z. physik. Chem.*, 1910, **74**, 641.

TABLE 20

*Titoff's Values for x/m with Coconut Shell Charcoal*¹

At $p = 10$ cm. Hg						
Temperature	- 79	- 23.5	0	30	80	151.5
H ₂	0.791	—	0.227	—	0.0607	—
N ₂	15.89	—	2.344	1.178	0.4688	0.1633
CO ₂	97.27 ²	—	30.41	15.89	4.920	1.062
NH ₃	—	112.20	69.02	29.24	7.96	2.77

At $p = 70.5$ cm. Hg						
Temperature	- 79	- 23.5	0	30	80	151.5
H ₂	5.346	—	1.483	—	0.391	—
N ₂	42.56	—	13.37	7.096	2.972	1.122
CO ₂	115.3 ²	—	64.57	43.65	20.32	6.194
NH ₃	—	155.6	134.6	97.27	36.14	10.26

sorption was almost proportional to the pressure. Travers³ found that at the temperature of liquid air the sorption of hydrogen was proportional to the cube root of the pressure. For the other gases, Titoff found that the values of $1/n$ diminished as the temperature was lowered. The values were as follows :⁴

Temperature	- 79	0	30	80	151.5
N ₂	0.461	0.847	0.893	0.923	0.967
CO ₂	0.086	0.368	0.491	0.700	0.871
NH ₃	—	0.300	0.582	0.786	(0.685)

The extent to which the data comply with the empirical equation is indicated by the straightness of the lines in figs. 16 (Chapter III, page 34) and 25⁵ for hydrogen and nitrogen, respectively. Titoff likewise noted the empirical relation that for any definite pressure the logarithm of the amount of sorption, x/m , diminished linearly with temperature. This is

¹ A. Titoff, *Z. physik. Chem.*, 1910, **74**, 674; A. de Hemptinne (*Bull. sci. acad. roy. Belgique*, (3), 1898, **36**, 155; *Z. physik. Chem.*, 1898, **27**, 429) found that charcoal sorbed six times as much hydrogen at -78°C . as at $+15^{\circ}\text{C}$.

² Data obtained at -76.5° .

³ M. W. Travers, *Proc. Roy. Soc. (London)*, A, 1906, **78**, 9; *Z. physik. Chem.*, 1907, **61**, 241; H. Freundlich, *Z. physik. Chem.*, 1907, **61**, 249.

⁴ A. Titoff, *Z. physik. Chem.*, 1910, **74**, 675.

⁵ A. Titoff, *Z. physik. Chem.*, 1910, **74**, 655, fig. 7.

almost exact for hydrogen (see fig. 26¹), but the similar curves for nitrogen and carbon dioxide are definitely convex and concave downwards, respectively.

Miss Homfray² measured the sorption of argon, nitrogen,

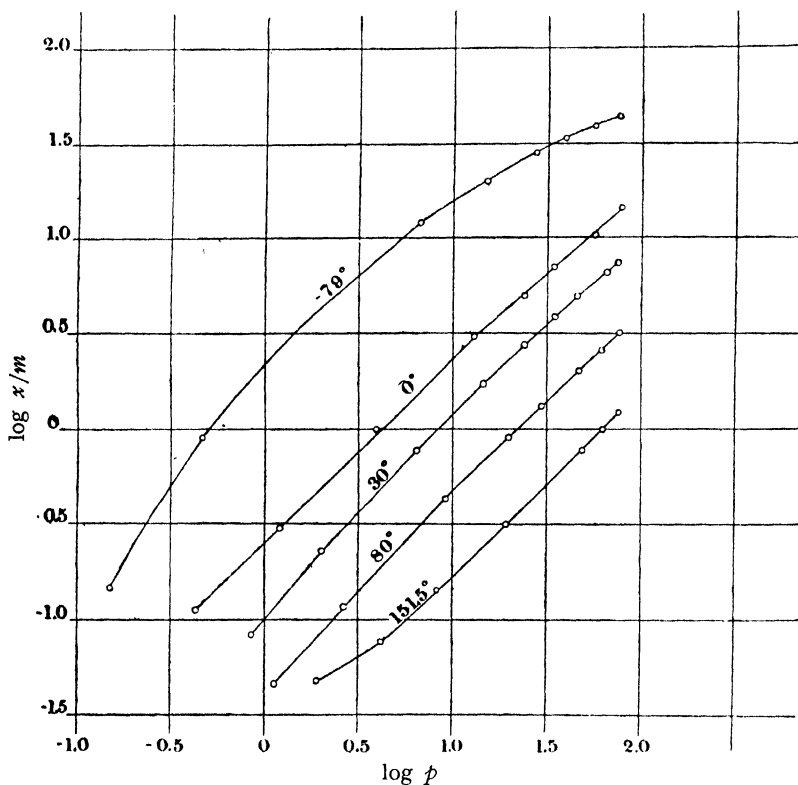


Fig. 25.—Titoff's data for the Sorption of Nitrogen by Charcoal graphed according to the Empirical Sorption Isotherm.

carbon monoxide, methane, ethylene, carbon dioxide, oxygen, helium and also mixtures of nitrogen and carbon monoxide, hydrogen and oxygen at temperatures from -190°C . to

¹ A. Titoff, *Z. physik. Chem.*, 1910, **74**, 652, fig. 5.

² I. F. Homfray, *Z. physik. Chem.*, 1910, **74**, 129.

+ 182° C. The charcoal had been heated for five hours and then extracted with nitric acid ; before use it was heated at 240° in a vacuum maintained by a Toepler mercury pump until no more gas was collected. Her sorption apparatus is shown in Chapter II, page 18, fig. 4.

Miss Homfray's results are summarized in comprehensive form in table 21 and fig. 27.¹ In all cases $C = \frac{100\ x}{m + x}$ per cent,

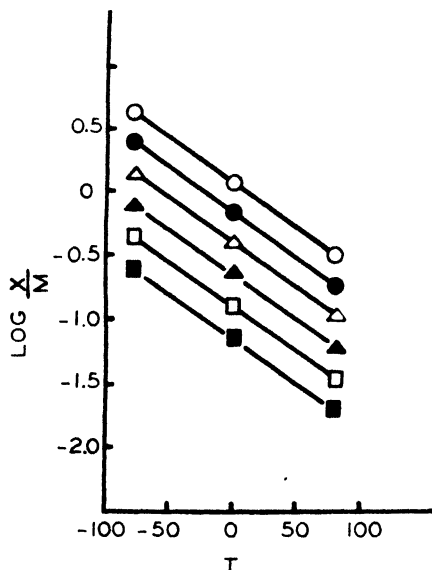


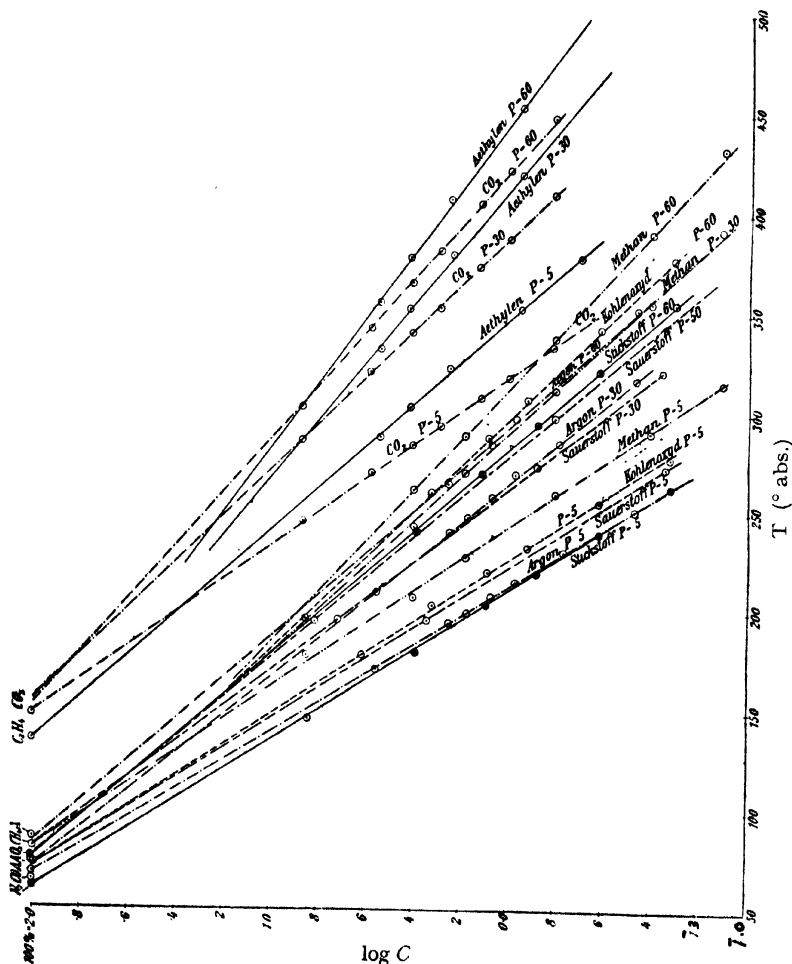
Fig. 26.—Isobars for the Sorption of Hydrogen by Charcoal at various Temperatures T (Titoff).

○— $p = 3.16$ ●— $p = 5.62$ △— $p = 10$
 ▲— $p = 17.78$ □— $p = 31.62$ ■— $p = 56.23$

where x is the weight of gas sorbed by m grams of charcoal. The heat of sorption q is calculated from the slopes of the isosteres, and when divided by the difference in temperatures for which C is 10 per cent and 1 per cent, a constant is obtained as shown in the last column. The difference in temperature

¹ I. F. Homfray, *Z. physik. Chem.*, 1910, **74**, 149, fig. 4.

Fig. 27.—Miss Homfray's Isobars for various Gases at three indicated pressures, $p = 5, 30$ and 60 cm. Hg, over a range of Temperature from -190° to $+182^{\circ}$ C. The points at the top of the Diagram refer to pure Liquefied Gas or Vapour with no Charcoal. Charcoal free from Sorbed Material would lie at an infinite distance below the Diagram. The Ordinates are $\log C$, where $C = \frac{100x}{m+x}$ per cent by weight. With remarkably close approximation, the Temperature for which the Sorption is 10 per cent is half-way between the Temperature for which the Sorption is 1 per cent and the boiling Temperature of the pure liquid at the same Pressure.



just referred to is shown to be parallel to the values of the molar refractions of the respective substances.

TABLE 21 ¹

Miss Homfray's Comparative Data for the Physical Properties of Various Gases and for their Sorption by Coconut Shell Charcoal.
All the Data Refer to a Pressure of 5 cm. Hg.

Gas.	Mol. wt.	Boiling pt. at 5 cm. Hg, °Abs.	C.c. (at N.T.P.) sorbed when C = 1%	Abs. temp. for C = 1%	Abs. temp. for C = 10%	q/diff. ²
			C = 1%	C = 1%	C = 10%	
N ₂	28	60	8.0	211	136	57
A	40	67	5.6	213.5	140	54
O ₂ ³	32	70	8.0	221	145	61
CO	28	64	13.1	227	147.5	68
CH ₄	16	80	5.0	242.5	161	77
CO ₂	44	146	7.5	318	233	68
C ₂ H ₄	28	135	7.0	345	240	69

For Miss Homfray's diagrams of isobars and isosteres for the individual gases studied the reader must be referred to the original paper. Here we reproduce but one diagram, fig. 28,⁴ showing the amounts of sorption of nitrogen at various temperatures and pressures.

Miss Homfray uses an empirical formula borrowed from the rule of Ramsay and Young to relate the effect of temperature upon sorption to the vapour pressure of any liquid; namely, $\frac{T_0}{T_1} - \frac{T'_0}{T'_1} = R(T_0 - T'_0)$, where T_1 and T'_1 are the absolute temperatures at any two pressures read from any one isostere ($x/m = \text{constant}$), T_0 and T'_0 are the absolute temperatures at which any saturated vapour has the same pressures, and R is some constant.

Hene⁵ gives the following table for the sorption of various gases by 1 gm. of Kahlbaum's "active charcoal" (for com-

¹ I. F. Homfray, *Z. physik. Chem.*, 1910, **74**, 194.

² Heat of sorption divided by the difference in the temperatures given in columns 5 and 6.

³ Results obtained mostly through calculation.

⁴ I. F. Homfray, *Z. physik. Chem.*, 1910, **74**, 167, fig. 9.

⁵ W. Hene, *Dissert.*, Hamburg, 1927, p. 21.

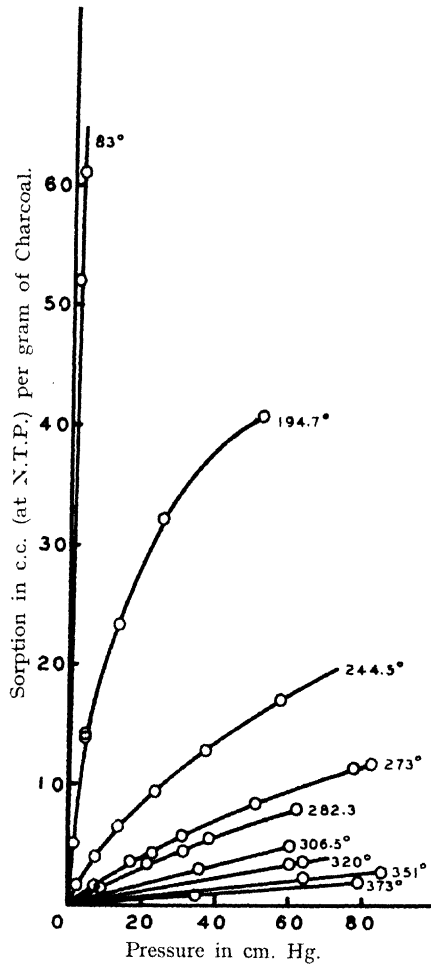


Fig. 28.—Isotherms for the Sorption of Nitrogen by Charcoal (Miss Homfray).

position see Chapter IV, page 77), previously heated in vacuo at 400°, the sorption being observed at 15° C. He obtained a fairly smooth parallelism with the boiling points and, par-

ticularly, critical temperatures of the respective gases. The influence of change in boiling point or critical temperature is much greater for the higher temperatures. Hene also gives a series of approximately determined isotherms and isobars together with graphs showing their relation to vapour pressures of the liquefied vapours.

TABLE 22

Sorption of Gases by One Gram of Kahlbaum's "Active Charcoal"

Gas	C.c. sorbed at 15° C.	Boiling pt. of gas, ° C.	Critical temp. of gas, ° C.
COCl ₂ . . .	440.0	+ 8.2	+ 183.0
SO ₂ . . .	379.7	— 10.1	+ 157.3
CH ₃ Cl . . .	277.0	— 24.0	+ 143.0
Cl ₂ . . .	234.6	— 33.7	+ 141-144
NH ₃ . . .	180.9	— 33.5	+ 132.4
H ₂ S . . .	98.9	— 61.7	+ 100.1
HCl . . .	72.0	— 83.0	+ 51.6
N ₂ O . . .	54.2	— 90.0	+ 36.0
C ₂ H ₂ . . .	48.9	— 84.0	+ 35.5
CO ₂ . . .	47.6	— 78.0	+ 31.3
CH ₄ . . .	16.2	— 164.0	— 86.7
CO . . .	9.3	— 190.0	— 140
O ₂ . . .	8.2	— 182.0	— 118
N ₂ . . .	8.0	— 195.0	— 146
H ₂ . . .	4.7	— 252.0	— 241

Howard and Hulett¹ obtained the following values in cubic centimetres at N.T.P. per gram of charcoal for the sorption at 25° by Ag99 coconut charcoal before and after the evacuated charcoal had been heated for half an hour at 1,200-1,300° C. in vacuo :

	CO ₂	N ₂	H ₂
Activated coconut shell charcoal . . .	51.0	8.2	0.81
Activated coconut shell charcoal after heating to 1,200-1,300° C. . .	25.6	3.9	0.55

It is significant that the decrease is least for the smallest molecule.

Hempel and Vater² observed that the ratio between the amounts of hydrogen and nitrogen sorbed was the same for

¹ H. C. Howard and G. A. Hulett, *J. Phys. Chem.*, 1924, **28**, 1094.

² W. Hempel and G. Vater, *Z. Elektrochem.*, 1912, **18**, 724.

coconut charcoal, kieselguhr, pumice and platinum black. It is therefore evident that the relative sorption of two such gases is more or less predictable. However, Sheldon¹ has found it possible to prepare charcoal by heating at 1,000° C. for 3½ hours (see pages 68 and 92) so that it is more active for hydrogen than for nitrogen, which we may explain as being due to the ultrapores becoming too small for the latter gas to penetrate.

Baerwald² naturally found that the ratio between the volumes of nitrogen and hydrogen sorbed depended upon the temperature as is shown by his measurements at one atmosphere (table 23). The charcoals were previously evacuated at 500° C. His paper also includes isobars for the gases of table 23 with the different charcoals.

TABLE 23

Volumes of Gas at 20° Sorbed at One Atmosphere by One Volume of Various Charcoals

Coconut (edible portion)						
Temp., ° C.	H ₂	N ₂	O ₂	Air	CO ₂	
+ 20	3.4	10.5	15.6	13.1	60	
- 185	131.5	158.0	173.3 (at - 162° C.)	165.7	110.0 (at - 40° C.)	
Elder pith						
	H ₂	Air.	N ₂	Coconut shell	Linden	
+ 20	.	.	3.24	—	37.5	19.0
- 185	.	.	153	262.3	235.0	104.5
						14.6
						220.7

Ratios between hydrogen and nitrogen sorbed by a number of materials are given in table 12, page 79. Similar results may be found in the early work of Joulin³ on nitrogen, hydrogen, oxygen and carbon dioxide. See also table 2 of Chapter III, page 38.

For ordinary active charcoal as used by Lemon and Blodgett,⁴ Wilson⁵ points out that 1.30 times as many molecules

¹ H. H. Sheldon, *Phys. Rev.*, (2), 1920, **16**, 165.

² H. Baerwald, *Ann. der Physik*, (4), 1907, **23**, 91, 95, 99, 101, 103.

³ L. Joulin, *Compt. rend.*, 1880, **90**, 741.

⁴ H. B. Lemon and K. Blodgett, *Phys. Rev.*, (2), 1919, **14**, 394.

⁵ R. E. Wilson, *Phys. Rev.*, (2), 1920, **16**, 8.

of oxygen as of nitrogen are sorbed at any given pressure. Even the rate of sorption of oxygen can be predicted from similar experiments with nitrogen. This ratio, 1.30, is likewise the ratio of close packed oxygen and nitrogen molecules as,

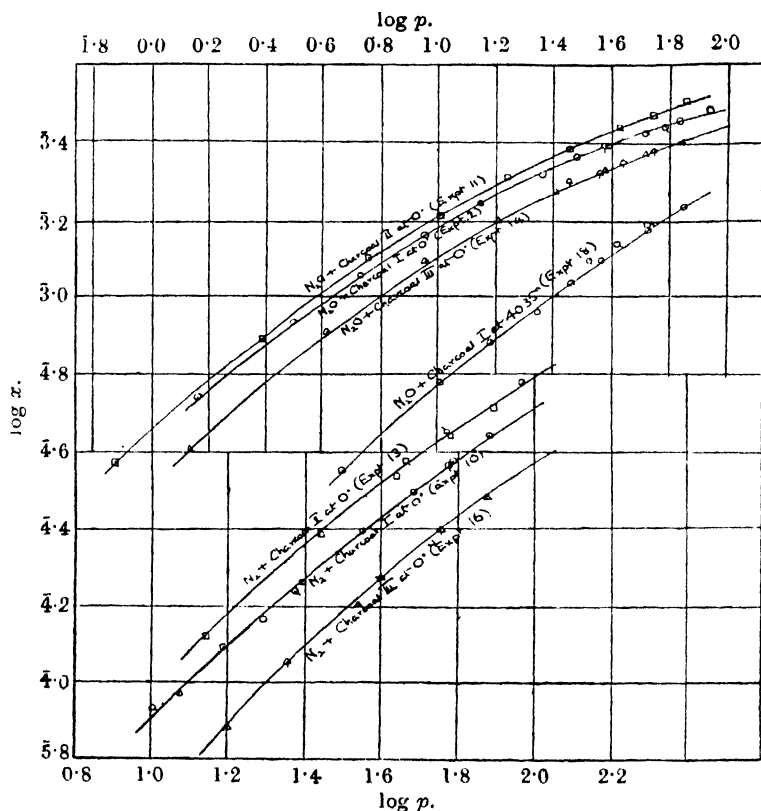


Fig. 29.—Sorption of Nitrogen and Nitrous Oxide by three Birchwood Charcoals (x is in gram mols per Gram of Charcoal).

for example, in the free liquids (1.31 at $-192^\circ C$). The rule applies even to mixtures of oxygen and nitrogen.

Hunter,¹ in Fontana experiments, had found that different charcoals sorb different proportions of various gases; namely,

¹ J. Hunter, *Phil. Mag.*, (4), 1863, **25**, 364.

ammonia, carbonic acid and cyanogen. Gregg,¹ however, found that three birchwood charcoals, evacuated at 10^{-4} mm. at 400° , sorb nitrogen, nitrous oxide and sulphur dioxide in the same order, as is shown for nitrogen and nitrous oxide

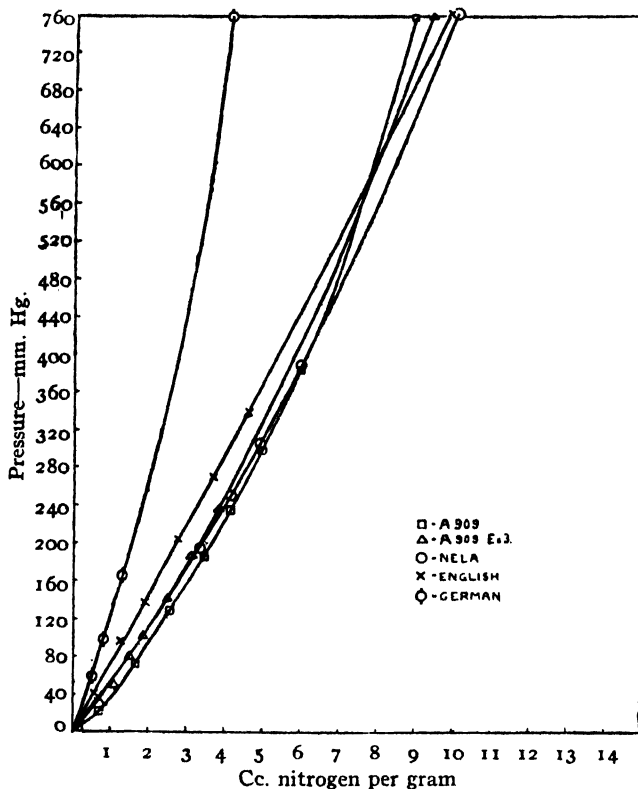


Fig. 30.—Lowry and Hulett's Isotherms for the Sorption of Nitrogen on Charcoals at 25° .

in his diagram here reproduced as fig. 29 (x is in gram mols. per gram of charcoal).

Careful measurements of the sorption of nitrogen and

¹S. J. Gregg, *J. Chem. Soc.*, **1927**, 1504. For his results with acetylene, ethane, carbon monoxide, carbon dioxide and ethylene, see Chapter XX, page 527.

carbon dioxide by various charcoals have been made by Lowry and Hulett,¹ whose results are given in figs. 30 and 31, which show the amounts in cubic centimetres at N.T.P.

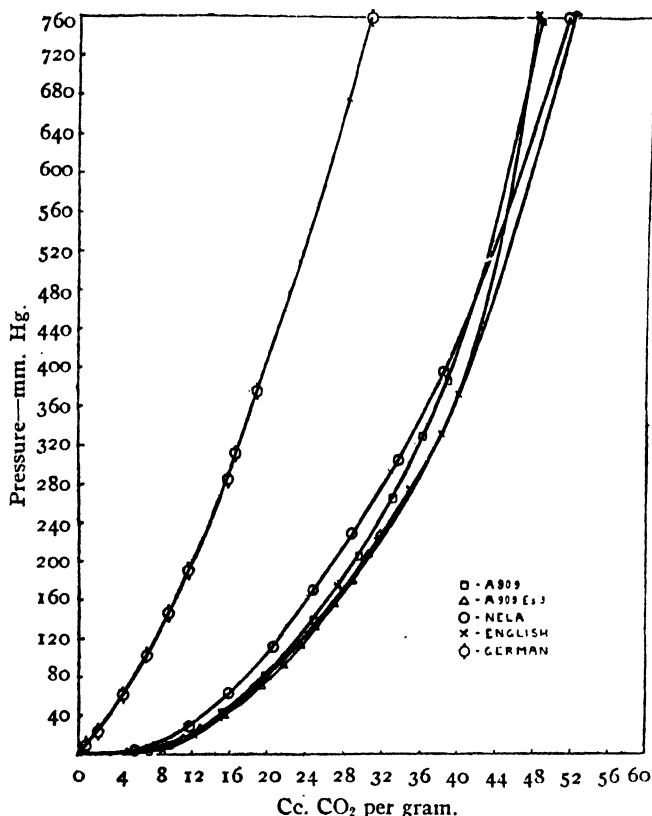


Fig. 31.—Lowry and Hulett's Isotherms for the Sorption of Carbon Dioxide on Charcoals at 25°.

sorbed per gram of charcoal at 25° C. The first three charcoals are steam activated coconut shell charcoal, the second specimen being very finely ground.

¹H. H. Lowry and G. A. Hulett, *J. Am. Chem. Soc.*, 1920, **42**, 1400, 1401, figs. 4 and 5.

EFFECT OF HIGH PRESSURES

The chief interest in the study of sorption under high pressures is in ascertaining whether sorption continues to increase with rise of pressure. It may do so or it may reach a constant "saturation" value unaffected by further increase of pressure. A third possibility,¹ so far not realized by experiment, is that the sorption should pass through a maximum and diminish at very high pressures.

Most of the work at pressures greater than atmospheric can be regarded only as semi-quantitative in view of the large uncertainty as to the amount of gas in the dead spaces of the apparatus. The early work of Hunter² and of Pfeiffer³ at pressures not exceeding 5 to 8 atmospheres exemplified the first possibility, continued increase in sorption. Dewar,⁴ on the other hand, found that at -185°C . charcoal sorbed at 1, 5, 10, 15, 20 and 25 atmospheres 92.5, 138.1, 156.7, 149.3, 145.5 and 138.1 c.c., respectively, of hydrogen measured at N.T.P. This he regarded as constant sorption over the whole range of higher pressures. Leprince-Ringuet's⁵ data were intermediate in character, although he carried the pressure to 80 atmospheres, using carbon dioxide, air, methane, oxygen and fire-damp with wood charcoal and various coals.

Graham's⁶ data for the sorption of methane, carbon dioxide and nitrogen by 200-mesh coal at 10.8°C . are shown in fig. 32 which gives the sorption in cubic centimetres (at N.T.P.) per 100 gms. of coal dust. It will be noticed that moist coal

¹ Compare H. Freundlich, *Kapillarchemie*, p. 172 (Akademische Verlagsgesellschaft, m.b.H., Leipzig, 1922); *Colloid and Capillary Chemistry*, p. 128 (Methuen & Co., Ltd., London, 1926).

² J. Hunter, *J. Chem. Soc.*, 1871, **24**, 76. Ammonia, cyanogen and carbon monoxide by charcoal in a Fontana experiment.

³ E. W. R. Pfeiffer, *Dissert.*, Erlangen, 1882. Compare *Beibl. Ann. Physik*, 1884, **8**, 630. Ammonia and carbon dioxide by glass wool or charcoal and glass wool.

⁴ J. Dewar, *Proc. Roy. Inst. Gr. Brit.*, 1906, **18**, 437.

⁵ F. Leprince-Ringuet, *Compt. rend.*, 1914, **158**, 573.

⁶ J. I. Graham, *Colliery Guardian*, 1921, **122**, September 16, p. 810, fig. 4.

sorbed about one-third as much as dry. Briggs and Cooper¹ attempted to increase the capacity of storage cylinders for highly compressed gas by filling them with charcoal or silica, using nitrogen, oxygen and hydrogen at 15° C. in some cases up to 100 atmospheres. They tested activated birch charcoal, German impregnated charcoal and wood charcoal. At 35 atmospheres the capacity of a cylinder for nitrogen was increased 66 per cent by filling with coconut charcoal. At higher pressures the increase in capacity gradually disap-

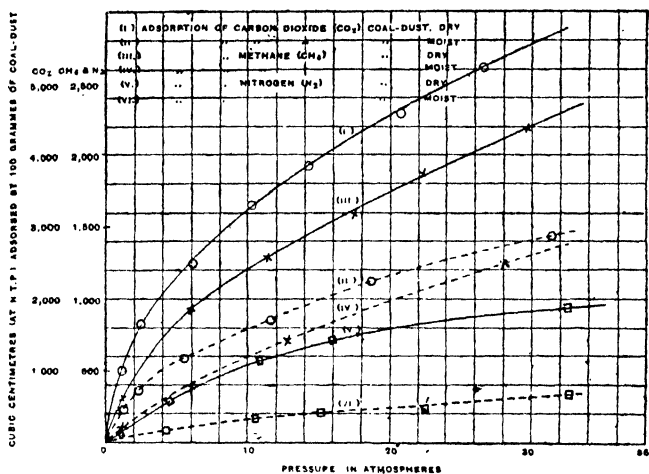


Fig. 32.—Sorption of Gases under High Pressures by 200-mesh Coal Dust at 10.8° C. (Graham).

peared. Some of their results are shown in fig. 33 which gives the amounts of gas measured at 1 atmosphere and 15° C. forced into 1 litre of granules. It is of interest to note that, contrary to Dewar's observations at -185° C., but quite in accordance with expectations, the sorption of hydrogen was steadily increasing over the whole range of pressures at room temperature. This follows from the concept of persorption (Chapter IV, page 64), since so much more hydrogen is taken up even at low pressures at the lower temperature.

¹ H. Briggs and W. Cooper, *Proc. Roy. Soc. Edin.*, 1921, **41**, 119.

Quantitative measurements of the effect of high pressure have been obtained by the use of the McBain-Bakr sorption balance. McBain and Britton ¹ have studied the sorption of nitrogen, nitrous oxide and ethylene at pressures up to 60 atmospheres. The results are of especial interest in that, being carried out with a permanent gas and with vapours above and below critical temperatures and pressures, they

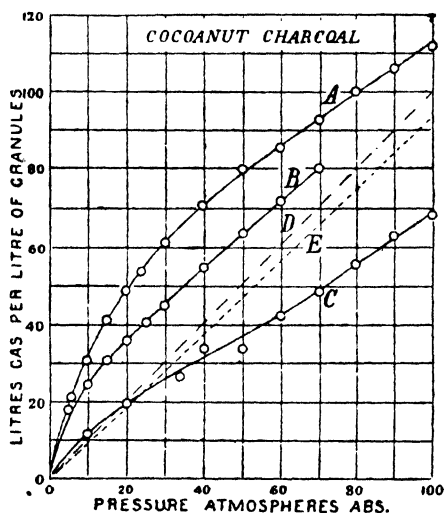


Fig. 33.—A—Sorption Isotherm for Nitrogen ; B—Sorption Isotherm for Hydrogen ; C—Sorption Isotherm for Nitrogen with Damp Charcoal ; D—Simple Compression according to Boyle's Law ; E—Simple Compression for Hydrogen.

enable a decision to be reached between rival views as to the nature of sorption by charcoal.

Two specimens of activated sugar charcoal were used, the one being treated with steam at 700° ("Steam D") and the other partially oxidized with air at 1,140° C. ("Air C"). Preliminary evacuation at 450° was carried out at less than 10^{-4} mm. Hg for four or five hours and repeated after admission of the gas in question.

¹ J. W. McBain and G. T. Britton, *J. Am. Chem. Soc.*, 1930, **52**, 2198.

One of the most interesting findings is that the first half of the total sorbed material is taken up at low pressures, almost infinitesimal in the cases of nitrous oxide and ethylene. This is clearly shown by figs. ¹ 34, 35 and 36 when it is remembered that all curves must begin in the origin of the diagram.

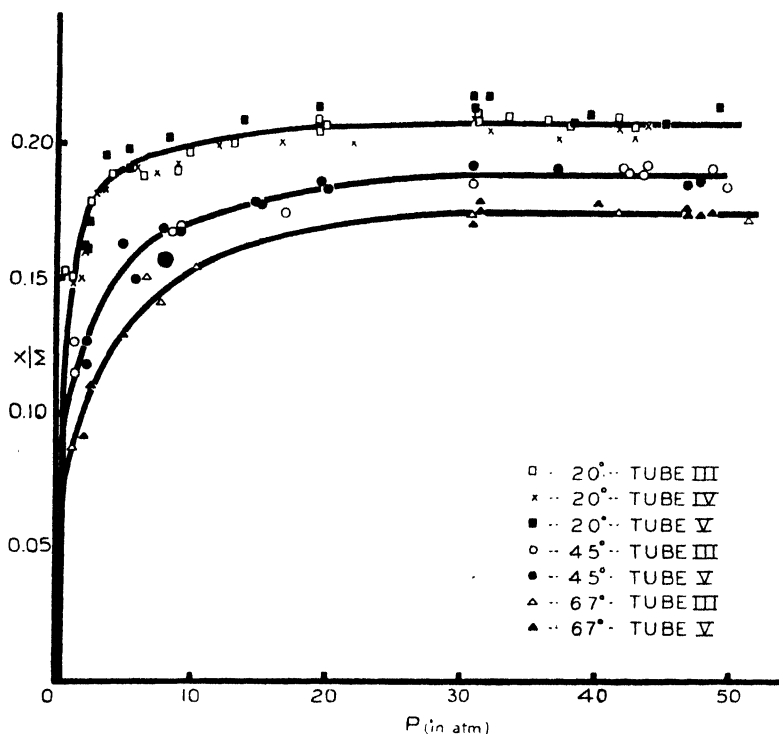


Fig. 34.—Isotherms for the Sorption of Nitrous Oxide by Steam Activated Sugar Charcoal.

The data portray true reversible equilibria, because points on the curve obtained by sorption or by desorption are indistinguishable within the experimental error. The curves for gases and vapours are similar, and no special difference is

¹ J. W. McBain and G. T. Britton, *J. Am. Chem. Soc.*, 1930, **52**, 2214 and 2215, figs. 9, 10 and 11.

noticed when studying nitrous oxide and ethylene above and below their critical temperatures. The critical temperatures and pressures of ethylene and nitrous oxide are 9.2° and

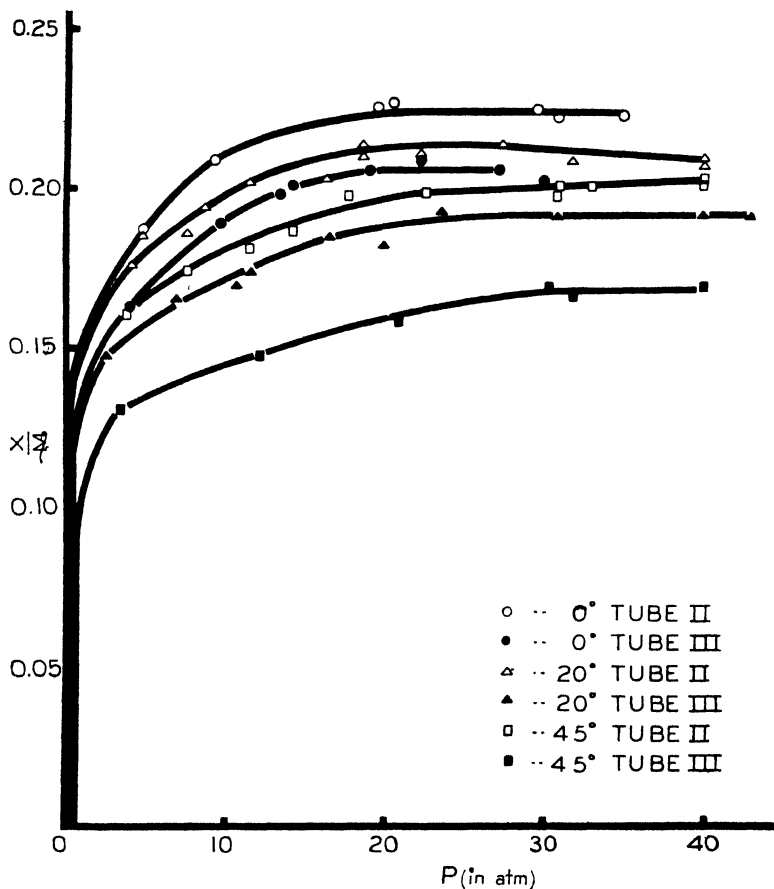


Fig. 35.—Isotherms for the Sorption of Ethylene by Air Activated Sugar Charcoal.

58 atmospheres, and 38.8° and 77.5 atmospheres, respectively. Several other authors¹ have noted that sorption curves above

¹ For example, H. Baerwald (*Ann. der Physik*, (4), 1907, **23**, 87) using carbon dioxide with coconut charcoal.

and below the critical temperature are very similar, although they refer to gas and vapours respectively.

In the higher regions of pressure the buoyancy correction for the density of the gas or vapour becomes important. This is clearly shown by the data in table 24, where neglect

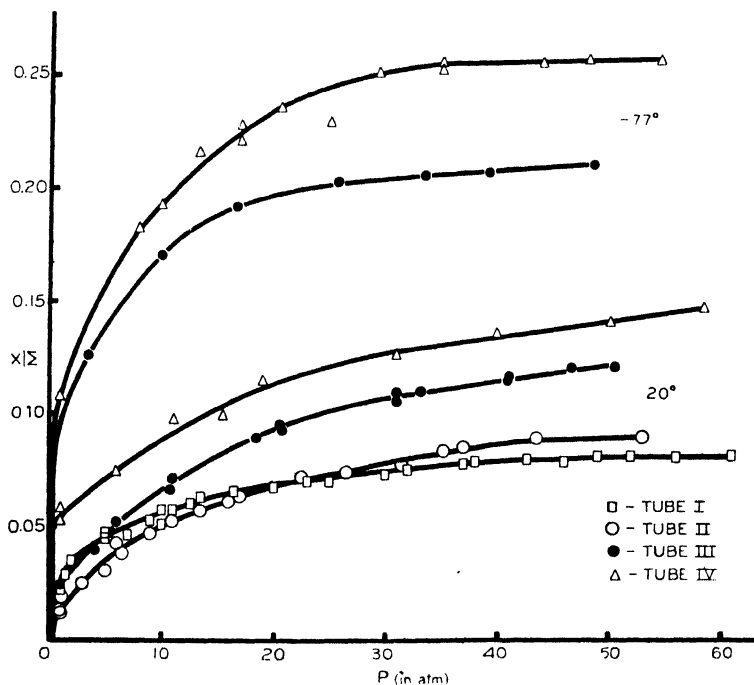


Fig. 36.—Isotherms for the Sorption of Nitrogen by Charcoal. Steam Activated Sugar Charcoal was used in Tubes I and II and Air Activated in Tubes III and IV.

of the buoyancy correction causes the uncorrected values of the sorption x to pass through a maximum and then fall off with further increase of pressure. In the following table T is the temperature of the liquid nitrous oxide, p is the corresponding vapour tension in atmospheres, x uncorrected is the apparent weight of gas sorbed by 0.10238 of charcoal, x cor-

rected is the weight sorbed after correcting for buoyancy, and x/m is the sorption in grams per gram of charcoal.

TABLE 24

Sorption of Nitrous Oxide by 0.1023 g. Steam Activated Sugar Charcoal at 20°C.

$T, ^\circ\text{C.}$	$p, \text{atm.}$	x (uncorr.), g.	x (corr.), g.	x/m
- 96.5	0.6	0.01554	0.0156	0.153
- 87.0	1.1	0.01528	0.0154	0.151
- 72.5	2.4	0.01797	0.0182	0.178
- 62.0	4.0	0.01889	0.0194	0.189
- 50.5	6.3	0.01849	0.0192	0.188
- 41.5	8.8	0.01836	0.0195	0.190
- 39.0	9.7	0.01895	0.0202	0.197
- 30.5	13.0	0.01882	0.0205	0.201
- 18.0	19.3	0.01823	0.0210	0.205
- 18.0	19.3	0.01823	0.0210	0.205
- 18.0	19.3	0.01869	0.0214	0.210
- 17.0	19.8	0.01830	0.0211	0.207
+ 0.5	31.1	0.01672	0.0217	0.212
+ 0.5	31.1	0.01646	0.0214	0.209
+ 3.8	33.4	0.01613	0.0216	0.211
+ 7.4	36.3	0.01528	0.0214	0.209
+ 9.4	38.0	0.01475	0.0213	0.208
+ 12.9	41.6	0.01410	0.0215	0.210
+ 13.9	42.8	0.01344	0.0212	0.207

After correcting for buoyancy, all the experiments with nitrous oxide and ethylene exhibited a saturation value at the higher pressures, whereas with nitrogen the saturation value was observed only for the steam activated charcoal. However, the data for the sorption of nitrogen indicate that if higher pressures had been employed, appreciably more sorption would have taken place and a saturation value might have been reached even with the air activated charcoal.

Frolich and White¹ have recently measured the sorption of hydrogen and methane and their mixtures by "activated charcoal" at pressures up to 140 atmospheres. The sorptive capacity approached the saturation value at 80-100 atmospheres except for hydrogen at higher temperatures, and the sorption of hydrogen at 120 atmospheres became negligible at 150°.

¹ K. Frolich and A. White, *Ind. Eng. Chem.*, 1930, **22**, 1058.
S.G.V.

The theoretical conclusions which may be derived from all the foregoing data and their conformity with the Langmuir rather than other formulations will be discussed in Chapters XVII and XVIII.

SORPTION OF CARBON DIOXIDE AND AMMONIA

Of all gases carbon dioxide is the one whose sorption has been most often studied. In Chapter I, figs. 1, 2 and 3 reproduce some of the most accurate isotherms for this gas.¹ Other data by Baerwald have already been quoted in this chapter, page 103. There is no obvious indication of the formation of any special compound as in the case of oxygen and carbon;² instead, results are rather similar to those with ammonia.

Earlier work was summarized by Wilhelm Ostwald,³ whose diagram is reproduced in fig. 37, which gives the logarithm of the amount of sorption, x/m , plotted against the logarithm of the pressure. It includes the accurate work of Chappuis⁴ in addition to that of Kayser⁵ and Joulin.⁶

¹ I. F. Homfray, *Z. physik. Chem.*, 1910, **74**, 129; A. Titoff, *Z. physik. Chem.*, 1910, **74**, 641; L. B. Richardson, *J. Am. Chem. Soc.*, 1917, **39**, 1828.

² L. B. Richardson, *J. Am. Chem. Soc.*, 1917, **39**, 1845; but H. S. Taylor and H. A. Neville (*J. Am. Chem. Soc.*, 1921, **43**, 2069) explain catalysis as being due to the reversible formation of a compound C_xO_y .

³ Wilhelm Ostwald, *Lchrbuch der allgem. Chemie*, 2 Aufl., Bd. II, Abt. 3, p. 233 (1906).

⁴ P. Chappuis, *Wied. Ann. der Physik*, 1881, **12**, 161. Chappuis also measured points on the following isotherms at 0° C.: ammonia by charcoal and asbestos; sulphur dioxide by charcoal, meerschaum, platinum black and rubber; and carbon dioxide and air by charcoal (*Wied. Ann. der Physik*, 1883, **19**, 27); the highest values for sulphur dioxide in cubic centimetres per gram of solid were 93 for charcoal, 67 for meerschaum of specific gravity 2.76, 2 for platinum black, 41 for black rubber and negligible amounts for asbestos and pumice. To this list may be added 0.07 c.c. for platinum sponge (G. Magnus, *Pogg. Ann. der Physik*, 1853, **89**, 609).

⁵ H. Kayser, *Wied. Ann. der Physik*, 1881, **12**, 526 (sulphur dioxide, carbon dioxide, air and hydrogen by evacuated boxwood charcoal).

⁶ L. Joulin, *Ann. chim. phys.*, (5), 1881, **22**, 398.

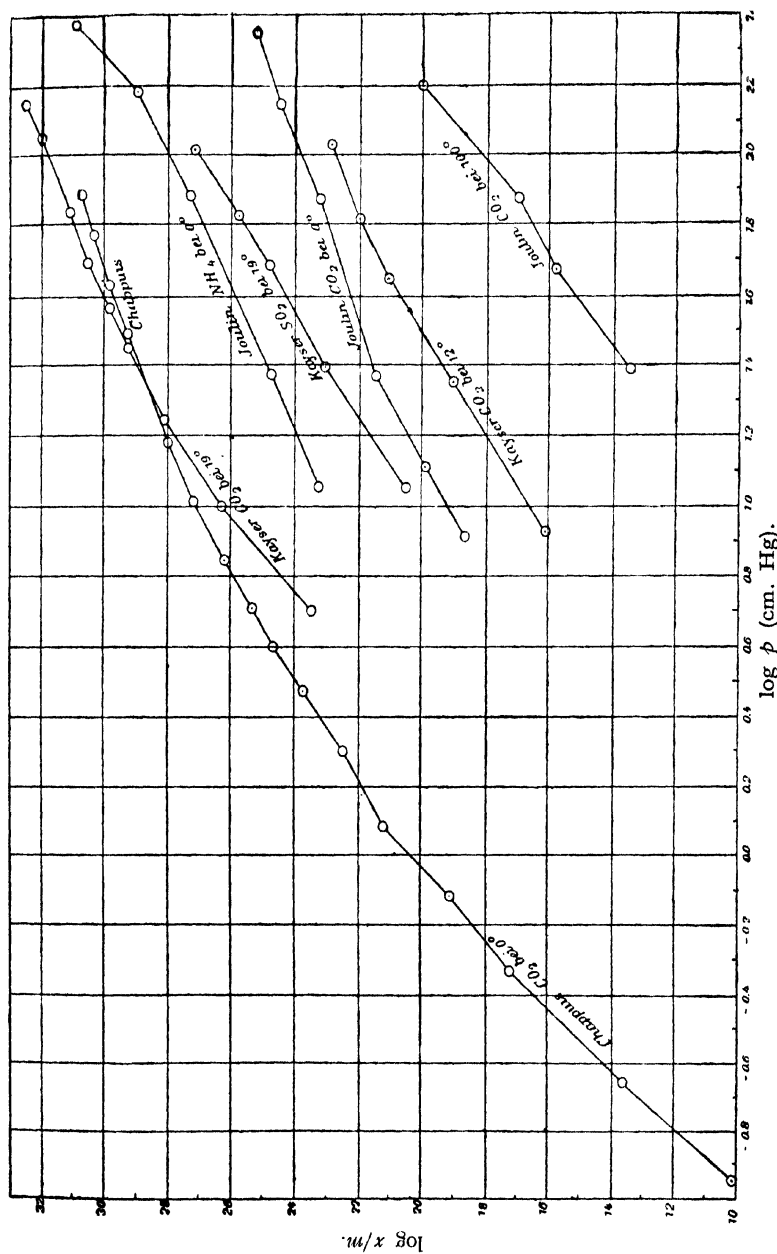


Fig. 37.—Sorption of Carbon Dioxide, Sulphur Dioxide and Ammonia by Charcoal.

Travers' results¹ for carbon dioxide were shown graphically in Chapter II, page 29, fig. 12. From the slope of the graphs there given it is apparent that the value of $1/n$ is such that at 100°C . the sorption is proportional to the square root of the pressure and at 0°C . is proportional to the cube root of the pressure.

Miss Homfray's isosteres for constant amounts of sorption

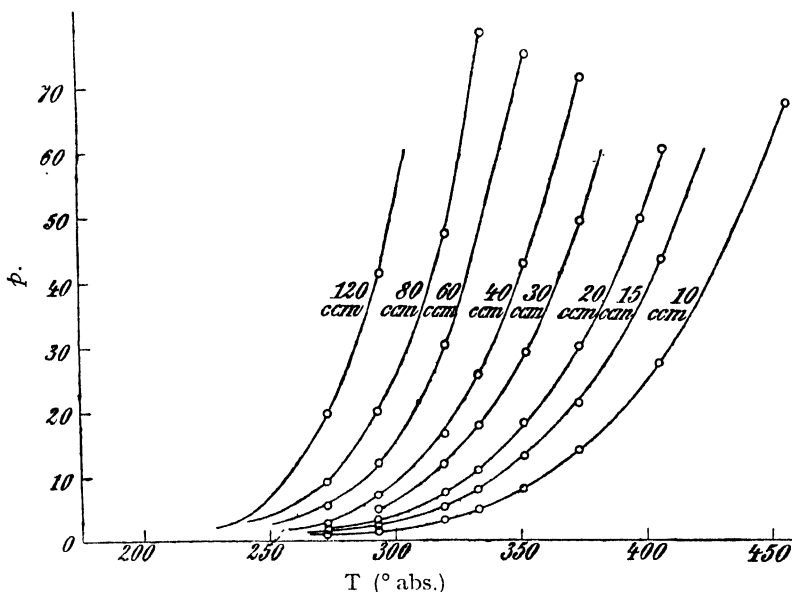


Fig. 38.—Miss Homfray's Isosteres for Constant Amounts of Sorption of Carbon Dioxide by Charcoal.

of carbon dioxide at various temperatures and pressures are given in fig. 38.² Richardson's results for carbon dioxide are given in logarithmic form in fig. 39,³ while those for ammonia

¹ M. W. Travers, *Proc. Roy. Soc. (London)*, A, 1906, **78**, 9; *Z. physik. Chem.*, 1907, **61**, 241; H. Freundlich, *Z. physik. Chem.*, 1907, **61**, 249.

² I. F. Homfray, *Z. physik. Chem.*, 1910, **74**, 186, fig. 18. Adsorption is measured at N.T.P. for 2.964 g. of charcoal.

³ L. B. Richardson, *J. Am. Chem. Soc.*, 1917, **39**, 1843, fig. 6.

have been shown graphically in Chapter II, page 30, fig. 13. Time effects with carbon dioxide were noted by him and by Rowe¹ and Sameshima.²

Magnus and his co-workers³ encountered an obvious source of error when studying the sorption of carbon dioxide by charcoal which had been heated to various temperatures.

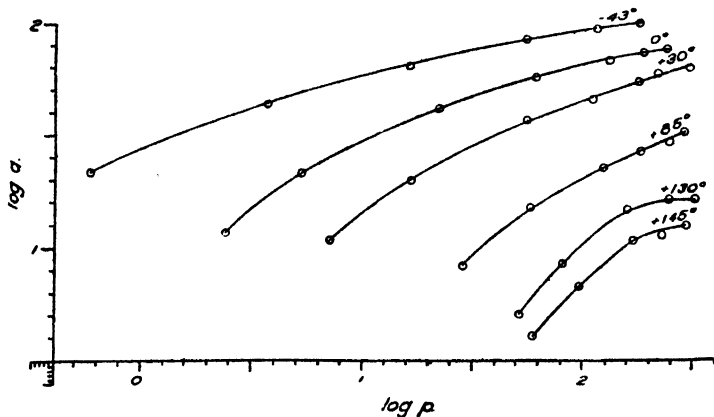


Fig. 39.—Richardson's Isotherms for the Sorption of Carbon Dioxide by Charcoal (a = Volume of Gas at N.T.P. Sorbed by 1 Gram of Charcoal).

Especially at low pressures there were discrepancies. These were found to be due to calcium carbonate, which is decomposed into calcium oxide on heating. Extraction of the charcoal with strong acids removes the discrepancies both in the

¹ H. Rowe, *Phil. Mag.*, (7), 1926, **1**, 659.

² J. Sameshima, *Bull. Chem. Soc. Japan*, 1927, **2**, 1; carbon dioxide by many charcoals and isotherms at various temperatures by bamboo charcoal.

³ A. Magnus and L. Cahn, *Z. anorg. allgem. Chem.*, 1926, **155**, 205; A. Magnus, E. Sauter and H. Kratz, *Z. anorg. allgem. Chem.*, 1928, **174**, 142; A. Magnus and H. Kratz, *Z. anorg. allgem. Chem.*, 1929, **184**, 241. Similarly, A. S. Coolidge (*J. Am. Chem. Soc.*, 1927, **49**, 710) found that sulphur dioxide was retained by coconut charcoal from which the ash had not been removed. This is probably also the explanation of the anomalous results published by M. Polányi and K. Welke, *Z. physik. Chem.*, 1928, **132**, 371 (see Chapter III, page 39).

pressure relationships and the initial heats of sorption. At low pressures the sorption is then proportional to the pressure up to 3 mm. They also compared the sorption of ammonia and carbon dioxide by beechwood and coconut charcoal and by natural and Acheson graphite.

Like Miss Homfray, Sameshima¹ regarded the sorption of carbon dioxide as solid solution in charcoal, although Henry's law did not apply. Just because Henry's law did apply in experiments at 20° with Kahlbaum's blood charcoal (6.49 per cent ash), Reyckler² drew the conclusion that the carbon dioxide molecules in canals and crevices had a similar environment to carbon dioxide molecules in solid solution in charcoal, which comes near to the present conception of persorption and the views of Coolidge.³

It is well to be reminded that the sorptive powers of various charcoals for ammonia and carbon dioxide do not always go hand in hand. This is well brought out in the following table from Stenhouse.⁴ Taylor, Neville and Burns⁵ find that

TABLE 25
Cubic Centimetres of Gases Sorbed by One Gram of Charcoal

	NH ₃	HCl ⁶	CO ₂
Wood charcoal	145	159	15
Animal charcoal	105	—	2.5
Purified animal charcoal	210	185	0
Wood charcoal impregnated with 7½% Al ₂ O ₃	212.5	177.5	12.5
Wood charcoal impregnated with 7½% CaHPO ₄	152.5	—	10
Pure charcoal, from Ca(OH) ₂ and tar	335	130	0
Charcoal with 5% platinum	142.5	135	0

¹ J. Sameshima, *Bull. Chem. Soc. Japan*, 1927, **2**, 1; carbon dioxide by many charcoals and isotherms at various temperatures by bamboo charcoal.

² A. Reyckler, van Bemmelen's *Gedenkboek*, 1910, p. 55. Also A. Reyckler, *J. Chim. Phys.*, 1910, **8**, 617.

³ A. S. Coolidge, *J. Am. Chem. Soc.*, 1926, **48**, 1795. See also J. Sameshima, *Bull. Chem. Soc. Japan*, 1929, **4**, 125; *Chem. News*, 1929, **139**, 61. (Carbon dioxide by various charcoals.)

⁴ J. Stenhouse, *Ann. der Chem. u. Pharm.*, 1857, **101**, 243.

⁵ H. S. Taylor, H. A. Neville and R. M. Burns, *J. Am. Chem. Soc.*, 1921, **43**, 2070.

⁶ See also W. D. Bancroft and C. E. Barnett, *J. Phys. Chem.*, 1930, **34**, 497.

certain additions to charcoal may increase the sorptive power for carbon dioxide by as much as a dozen-fold, probably through chemical action.

Others who have measured or compared the sorption of carbon dioxide and ammonia include Hunter,¹ Giesen,² Firth,³ Herbst,⁴ Longinescu and Theodosiu,⁵ Henglein and Grzenkowski,⁶ Shiels,⁷ Pearce and Knudson,⁸ and the more extensive work of Ruff and Hohlfeld⁹ and of Ruff and Roesner.¹⁰ See also Chapter IV, page 124, fig. 40, and the work of Coolidge;¹¹ also the graphs of Schmidt,¹² Chapter III, page 56, fig. 23. Sulphur dioxide was studied at -10°C . by Williams.¹³

¹ J. Hunter, *J. Chem. Soc.*, 1871, **24**, 76; 1872, **25**, 649. (Coconut charcoal with ammonia, carbon dioxide, cyanogen, hydrogen and nitrogen.)

² J. Giesen, *Ann. der Physik*, (4), 1903, **10**, 830. (Air, carbon, dioxide and ammonia on charcoal by the Salvioni micro-balance.)

³ J. B. Firth, *J. Chem. Soc.*, 1921, **119**, 926. (Ammonia by coconut charcoal after various heat treatments.)

⁴ H. Herbst, *Biochem. Z.*, 1921, **115**, 204. (Carbon dioxide by various materials including wood before and after carbonization and further treatments.)

⁵ G. G. Longinescu and C. N. Theodosiu, *Bul. chim. soc. Romana Stiinta*, 1924, **27**, Nos. 1-8. (Demonstrations of sorption of ammonia, hydrochloric acid, benzene, ether, carbon disulphide, etc., by vegetable charcoal.)

⁶ F. A. Henglein and M. Grzenkowski, *Z. angew. Chem.*, 1925, **38**, 1186. (Ammonia, sulphur dioxide and chlorine by commercial charcoal up to six atmospheres.)

⁷ D. O. Shiels, *J. Phys. Chem.*, 1929, **33**, 1386. (Carbon dioxide, nitrous oxide and sulphur dioxide by German gas-mask charcoal.)

⁸ J. N. Pearce and C. M. Knudson, *Proc. Iowa Acad. Sci.*, 1927, **34**, 197; C. M. Knudson, *Dissert.*, State University of Iowa, 1924.

⁹ O. Ruff and E. Hohlfeld, *Kolloid-Z.*, 1925, **36**, 29. (Ammonia, carbon dioxide and acetylene by steam activated alder-wood charcoal.)

¹⁰ O. Ruff and G. Roesner, *Ber.*, 1927, **60**, 411. (Argon, carbon dioxide, ammonia and sulphur dioxide by nine different kinds of charcoal, activated and non-activated.)

¹¹ A. S. Coolidge, *J. Am. Chem. Soc.*, 1927, **49**, 709.

¹² O. Schmidt, *Z. physik. Chem.*, 1928, **133**, 292; C_2H_4 , C_2H_6 , CO_2 , CH_4 , CO , N_2 , NH_3 , $\text{Ar} + \text{N}_2$, H_2 by charcoal (graphs only).

¹³ A. M. Williams, *Proc. Roy. Soc. Edin.*, 1917, **37**, 161. See also one isotherm at 15° , W. A. Patrick, *Dissert.*, Göttingen, 1914, p. 29. Also A. Reychler, *J. Chim. Phys.*, 1910, **8**, 617; (sulphur dioxide and carbon dioxide by blood charcoal.)

SORPTION OF CHLORINE, OXYGEN, AND OXIDES OF NITROGEN

Chlorine and especially oxygen deserve special mention because here the chemical possibilities usually predominate over the physical relations which have been stressed in the foregoing treatment of indifferent gases. (Compare, for example, this chapter, page 71.)

Schönbein¹ found that charcoal instantaneously sorbed chlorine with evolution of heat. Charcoal containing much chlorine did not smell of the latter but emitted fumes of hydrogen chloride in the air and yielded hydrochloric acid on extraction with water. On heating, chlorine was not recovered, but the charcoal decomposed potassium iodide and indigo and gave a blue colour to guaiacum tincture. A similar product was obtained by treating chlorine water with charcoal. Bromine could not be recovered from charcoal at 100° but was recoverable at a higher temperature.² One part of iodine in nine parts of charcoal did not give off a trace of iodine at 100° but turned guaiacum tincture blue.

Berthelot and Guntz³ confirmed the observation made by Melsens in 1873 that when hydrogen is passed over charcoal saturated with chlorine, heat is absorbed and the temperature falls. However, they found that for 1 mol of chlorine which combined with hydrogen to form hydrogen chloride, 7 mols of chlorine were being desorbed.

Bohart and Adams⁴ studied the dependence of the sorption of chlorine, and of the formation of hydrogen chloride by various charcoals, upon the moisture in the vapour and in the charcoal; those with the greatest chlorine capacity were the best catalysts for the reaction between chlorine and water.

Oxygen, as was shown in Chapter I, pages 3, 9, and 10,

¹ C. F. Schönbein, *Pogg. Ann. der Physik*, 1848, **73**, 326. A. P. Okatov (*Zhur. Prikladnoi Khim.*, 1929, **2**, 21) observed that of the chlorine sorbed by charcoal, 11 per cent was retained even after heating in a stream of air at 260°–280° C.

² Compare V. N. Krestinskii, *J. Russ. Phys.-Chem. Soc.*, 1926, **58**, 998.

³ M. Berthelot and A. Guntz, *Compt. rend.*, 1884, **99**, 7.

⁴ G. S. Bohart and E. Q. Adams, *J. Am. Chem. Soc.*, 1920, **42**, 523. See also H. Lux, *Dissert.*, Karlsruhe, 1923.

is sorbed just like nitrogen at low temperatures, although its sorption at room ¹ and higher temperatures is accompanied by distinctively chemical phenomena (see also Chapter IV, pages 69, including footnote 3, and 70, including footnote 1). For example, animal charcoal on which oxygen is sorbed oxidizes tincture of guiacum to the same blue colour as do MnO_2 or Pb_3O_4 , such charcoal being more effective than ozone, whereas wood charcoal with sorbed oxygen has no such property.² Many interesting catalytic oxidations are known, some of which have received intensive study.³

At 0° C. there is no indication of chemical interaction between charcoal and nitrous oxide, carbon dioxide or carbon monoxide.⁴ It is only above 200° that carbon dioxide begins to be reduced very slowly by charcoal and at about 290° that carbon monoxide and charcoal begin to form carbon dioxide.

Any description of the sorption of oxygen by charcoal

¹ See also S. McLean, *Trans. Roy. Soc. Canada*, (3), 1919, **13**, 195. (Air, oxygen, nitrogen, hydrogen and carbon dioxide by carbonized lignite, effects of temperature and moisture.)

² This is an important consideration in selecting charcoals for practical use; it depends also upon the mode and degree of activation. For similar behaviour and comparison with a large number of powders, including charcoals, see A. Kutzelnigg, *Ber.*, 1930, **63B**, 1753. Charcoal requires only a brief exposure to the air in order to become a potential source of carbon dioxide which may yield carbonic acid when the charcoal is exposed to aqueous solutions or may bind alkali. See N. Shilov (Schilow) and K. Chmutov (Tschmutow), *Z. physik. Chem.*, Abt. A., 1930, **148**, 233; N. Shilov, *Kolloid-Z.*, 1930, **52**, 107. These authors further state that the form and position of the isotherm for the sorption of hydrochloric acid by charcoal is conditioned by surface oxides.

³ F. Feigl, *Z. anorg. allgem. Chem.*, 1921, **119**, 305 (solutions of sulphides, iodides, chromite, sulphite, stannite, mercurous salt and oxalic acid); O. Warburg, *Pflüger's Arch. ges. Physiol.*, 1914, **155**, 547 (oxalic acid); O. Warburg and E. Negelein, *Biochem. Z.*, 1921, **113**, 257 (α -amino acids); O. Meyerhof and H. Weber, *Biochem. Z.*, 1923, **135**, 558 (hexoses, charcoal and hexose phosphates); H. Freundlich and Alf Bjercke, *Z. physik. Chem.*, 1916, **91**, 1 (phenylthiourea); E. K. Rideal and W. M. Wright, *J. Chem. Soc.*, 1925, **127**, 1347 (oxalic and malonic acids).

⁴ M. S. Shah, *J. Chem. Soc.*, **1929**, 2673.

inevitably leads to discussion of the wider field of the oxidation of charcoal by oxygen, the oxides of nitrogen and even carbon dioxide ¹ at higher temperatures, a subject which cannot be more than briefly mentioned here.

Wheeler and his co-workers ² have devoted much attention to the subject of the oxidation of coal and of charcoal. Francis and Wheeler ³ state :

“ the oxidation of coal takes place through the medium of an adsorbed layer, which almost immediately reacts with certain external groupings of the ulmin molecule, yielding water, carbon dioxide and carbon monoxide, and forming unstable oxygenated groupings at the point of attack. As the adsorbed layer enters into chemical combination with the coal, it is replaced by a fresh layer, the process being continuous so long as there are groupings remaining with which oxygen can combine at the temperature of experiment. The unstable oxygenated groupings formed are ultimately carboxylic in character and cause the coal-ulmin to become soluble in alkali. When the temperature of the coal is raised under vacuum, the oxygenated groupings that have been formed are decomposed, yielding water and the oxides of carbon, the oxygen contained in these being equal in quantity to that ‘fixed’ during the oxidation. The coal now has an increased capacity for retaining oxygen, beyond that due to the normal oxidation, commensurate with the amount removed during exhaustion. This process of revivification can be repeated many times, but the character of the products of decomposition at each successive exhaustion gradually changes, because groupings of slightly different character are attacked or decomposed.” ⁴

¹ M. S. Shah (*J. Chem. Soc.*, **1929**, 2675) finds that at 470° C. activated sugar charcoal neither sorbs nor reacts with either carbon dioxide or carbon monoxide.

² T. F. E. Rhead and R. V. Wheeler, *J. Chem. Soc.*, 1912, **101**, 831, 846; 1913, **103**, 461, 1210; R. V. Wheeler, *J. Chem. Soc.*, 1918, **113**, 945; F. V. Tideswell and R. V. Wheeler, *J. Chem. Soc.*, 1919, **115**, 895; 1920, **117**, 794; R. V. Wheeler, *Engineering*, 1923, **115**, 667; W. Francis and R. V. Wheeler, *J. Chem. Soc.*, 1925, **127**, 112, 2238; **1926**, 1410; **1927**, 2958.

³ W. Francis and R. V. Wheeler, *J. Chem. Soc.*, **1927**, 2964.

⁴ Compare also G. Coles and J. I. Graham, *Fuel in Science and Practice*, 1924, **3**, 384; O. Manville, *Compt. rend.*, 1906, **142**, 1190, 1523; S. McLean, *Trans. Roy. Soc. Canada*, (3), 1921, **15**, 84.

Lowry and Hulett¹ consider that Rhead and Wheeler's carbon-oxygen complex is essentially a stable solid oxide.² Shah³ much prefers to regard this oxygen as sorbed in a special state in accordance with the views of Langmuir⁴ and Keyes and Marshall.⁵

Most of the investigators cited have measured the rate of sorption of oxygen by charcoal at one or more temperatures. Lowry and Morgan⁶ found with ten different charcoals prepared from anthracite coal that the rate of oxidation of the sample at 450° was roughly proportional to the amount of hydrogen contained in the charcoal and to the extent of surface as calculated from their data on the sorption of water vapour.

Rideal and Wright⁷ have measured the rate of autoxidation of activated sugar charcoal suspended in water at 40° and 50° C. with spontaneous evolution of some of the carbon dioxide formed. The latter was a reaction of zero order, yielding 0.013 cu. mm. of oxygen per hour per milligram of charcoal at 40° C. and 0.023 cu. mm. at 50° C., whence the temperature coefficient was 1.8. The rate was independent of the pressure of the oxygen. Shah's results⁸ with six gases and activated sugar charcoal are shown in fig. 40. Ward and Rideal⁹ measured the sorption of oxygen by their

¹ H. H. Lowry and G. A. Hulett, *J. Am. Chem. Soc.*, 1920, **42**, 1417. See also H. E. Armstrong, *J. Soc. Chem. Ind.*, 1905, **24**, 473. The oxygen so combined amounted to between 1.7 and 3.8 per cent of the weight of the activated gas mask charcoal.

² See also B. C. Brodie, Liebig's *Ann. der Chem.*, 1873, **169**, 270; M. Berthelot, *Bull. soc. chim.*, 1876, **26**, 102.

³ M. S. Shah, *J. Chem. Soc.*, **1929**, 2692.

⁴ I. Langmuir, *J. Am. Chem. Soc.*, 1915, **37**, 1154; 1918, **40**, 1361.

⁵ F. G. Keyes and M. J. Marshall, *J. Am. Chem. Soc.*, 1927, **49**, 156.

⁶ H. H. Lowry and S. O. Morgan, *J. Am. Chem. Soc.*, 1924, **46**, 846.

⁷ E. K. Rideal and W. M. Wright, *J. Chem. Soc.*, 1925, **127**, 1350; also A. F. H. Ward and E. K. Rideal, *J. Chem. Soc.*, **1927**, 3119.

⁸ M. S. Shah, *J. Chem. Soc.*, **1929**, 2669, fig. 3.

⁹ A. F. H. Ward and E. K. Rideal, *J. Chem. Soc.*, **1927**, 3123; for the charcoals used, see Chapter IV, page 87.

charcoals at $0^{\circ}\text{C}.$, finding the amounts almost proportional to the pressure of oxygen, x/m being between 6 and 8 c.c. (at N.T.P.) per gram of charcoal at 40 mm. pressure.

Nitric oxide¹ is sorbed by charcoal at 0° , but almost half of the gas recovered by evacuation at that temperature consists of nitrogen. Upon continued evacuation as the temperature is increased a further amount of nitric oxide is recovered along with carbon dioxide and nitrogen up to $125^{\circ}\text{C}.$, above

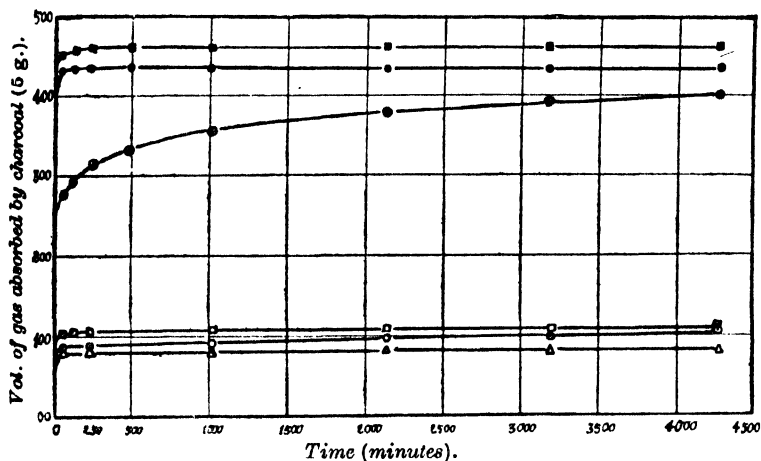


Fig. 40.—Shah's Isotherms for the Sorption of Various Gases by Charcoal at $0^{\circ}\text{C}.$; c.c. at N.T.P. ○—oxygen; ⊕—nitric oxide; ■—nitrous oxide; ●—carbon dioxide; □—carbon monoxide; △—nitrogen.

which no nitric oxide is obtained. Not until $280^{\circ}\text{C}.$ is reached is there much more recovery of gas and then it is a mixture of carbon dioxide and carbon monoxide. At 470° the behaviour of nitrous oxide resembles that just described for nitric oxide at 0° . In both these cases the oxide of nitrogen is held to the carbon by the oxygen atom and this arrangement may break up by liberation of the nitrogen with subsequent removal of carbon dioxide and carbon monoxide or it may come off intact. At $-190^{\circ}\text{C}.$ nothing can be removed when nitric

¹ M. S. Shah, *J. Chem. Soc.*, **1929**, 2661, 2676.

oxide is sorbed by charcoal; but at -78°C . some nitrogen and nitric oxide can be pumped off. It is often accompanied by nitrogen peroxide or, when the temperature is suddenly raised, by nitrogen trioxide. These possibilities are readily seen if it is assumed that the oxide of nitrogen can be sorbed upon oxygen already sorbed by the charcoal, as Shah supposes, or, as seems to the writer more probable, if the sorbed nitric oxide and oxygen are merely in intimate contact.

SORPTION OF VAPOURS

In discussing the sorption of vapours it is distinctly advantageous¹ to express pressures not in absolute units but in terms of relative humidity, p/p_s ; that is, the actual pressure, p , divided by the vapour pressure, p_s , of the corresponding liquid at the same temperature. p/p_s is often called the relative pressure, and it is upon this that the sorption of a vapour primarily depends.

The best work on the sorption of vapours apart from that carried out with the sorption balance appears to be that of Coolidge² and of Goldmann and Polányi.³ Fig. 41⁴ is Coolidge's representation of the general form of sorption curves for vapours. This assumes that the lower portion of the curve is in approximate agreement with the ordinary sorption isotherm, $x/m = kp^{1/n}$; whereas at higher values of

¹ F. T. Trouton and B. Pool, *Proc. Roy. Soc. (London)*, **A**, 1906, **77**, 292.

² A. S. Coolidge, *J. Am. Chem. Soc.*, 1924, **46**, 596. With a similar method J. N. Pearce and H. F. Johnstone (*J. Phys. Chem.*, 1930, **34**, 1260) have extended the measurements to methane, chlormethane, methylene chloride, chloroform and carbon tetrachloride. Their data are given only in graphical form, being expressed by double log isotherms and by isosteres. J. N. Pearce and A. L. Taylor (*J. Phys. Chem.*, 1931, **35**, 1091) have extended these measurements to include four alkyl chlorides (ethyl, n-propyl, n-butyl, and tertiary butyl); they discuss the effect of molecular weight and branching structure upon the increase in the time required for sorption, the amount of sorption and the reversal of the order of sorption (at 0°C . only) at sufficiently high pressures.

³ F. Goldmann and M. Polányi, *Z. physik. Chem.*, 1928, **132**, 321.

⁴ A. S. Coolidge, *J. Am. Chem. Soc.*, 1926, **48**, 1796, fig. 1.

x/m that relation ceases to hold, the curve becoming nearly straight, showing a rather sudden bend at the point marked *A* and appearing to terminate suddenly, having a finite slope at *B* where $p/p_s = 1$. The dashed line near *B* represents the rather indefinite results in the neighbourhood of saturated vapour.

Fleischer¹ adopts a somewhat similar curve, with points

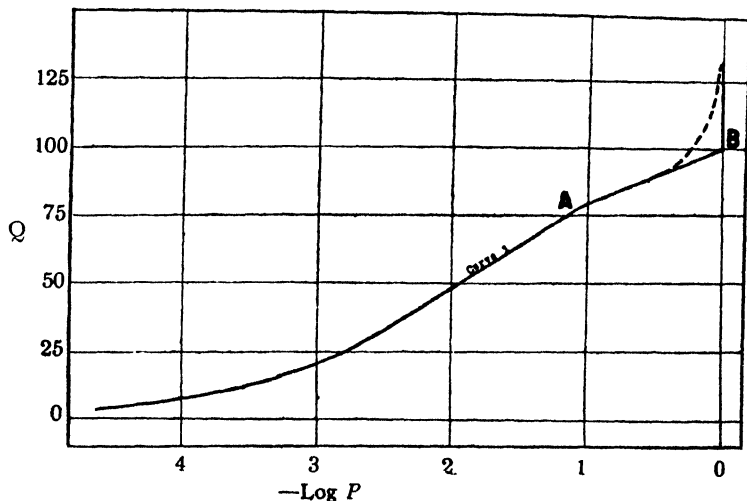


Fig. 41.—Coolidge's Typical Isotherm for the Sorption of a Vapour by Charcoal (*Q* is the Quantity Sorbed; *P* is the Relative Pressure).

of inflexion even more pronounced, for sorption of vapours by various materials. Freundlich's² typical curve is somewhat similar. Goldmann and Polányi's curves for the sorption of ethyl chloride and carbon disulphide by commercially activated charcoal, as plotted against the absolute pressure, are given in figs. 42 and 43.³ Their complete data are given, in different form, in Chapter XIV, pages 412–415, figs. 125–8.

¹ A. Fleischer, *Am. J. Sci.*, 1928, **16**, 247.

² H. Freundlich, *Kapillarchemie*, Bd. I, p. 233, fig. 40. Akademische Verlagsgesellschaft, m.b.H., Leipzig, 1930.

³ F. Goldmann and M. Polányi, *Z. physik. Chem.*, 1928, **132**, 342, figs. 9 and 10.

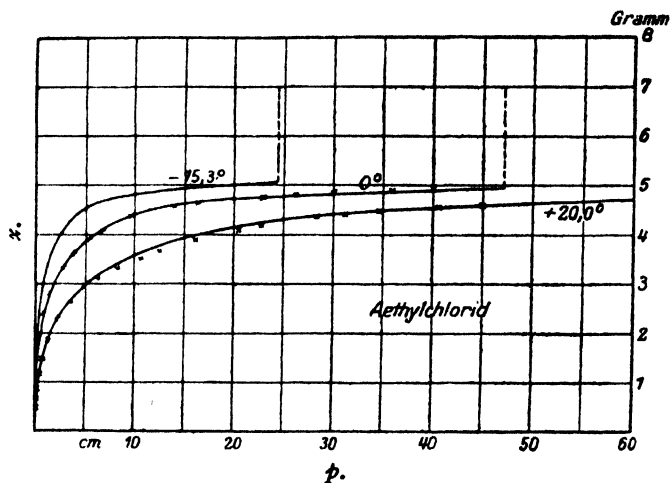


Fig. 42.—Goldmann and Polányi's Isotherms for the Sorption of Ethyl Chloride. x in Grams Sorbed per 10 g. Charcoal plotted against Pressures in cm. Hg.

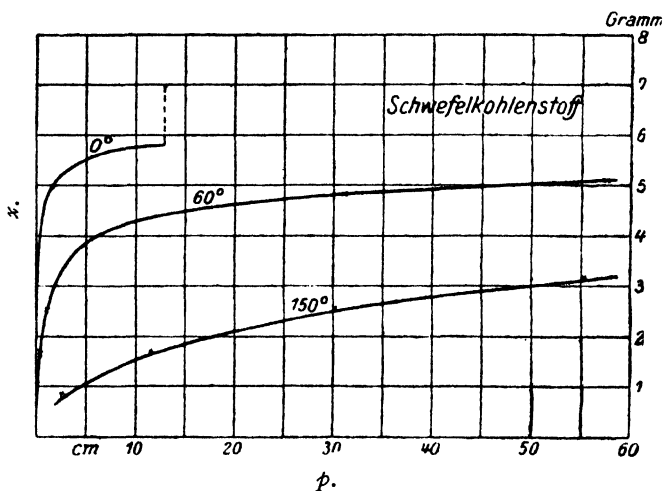


Fig. 43.—Goldmann and Polányi's Isotherms for the Sorption of Carbon Disulphide. x in Grams Sorbed per 10 g. Charcoal plotted against Pressures in cm. of Hg.

The use of the McBain-Bakr sorption balance in a sealed tube after rigorous evacuation and washing out the charcoal

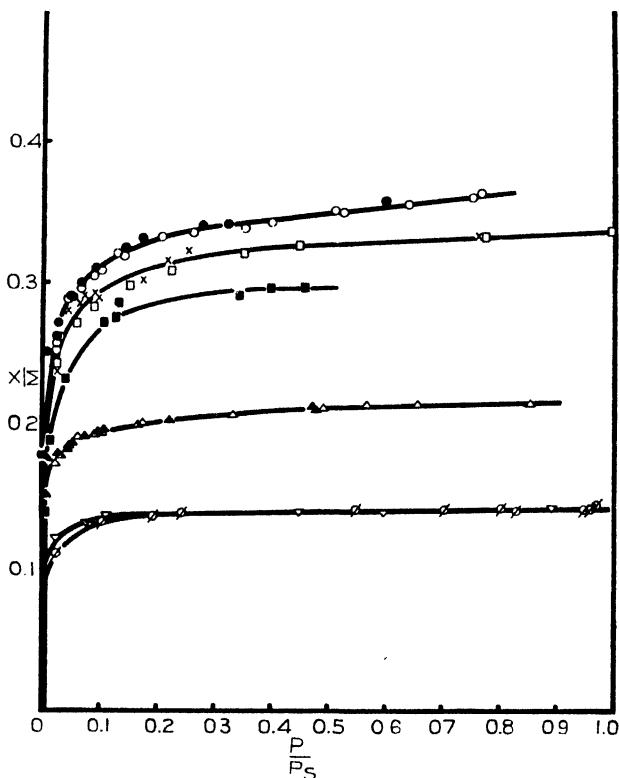


Fig. 44.—Isotherms for the Sorption of Toluene by various Activated Sugar Charcoals at 120° (■ — 205°).

with the vapour to be used ¹ (see Chapter II) has led the

¹ A. M. Bakr and J. E. King, *J. Chem. Soc.*, 1921, **119**, 454; A. M. Bakr and J. W. McBain, *J. Am. Chem. Soc.*, 1924, **46**, 2718; J. W. McBain, *Nature*, 1926, **117**, 550; J. W. McBain and G. T. Britton, *J. Am. Chem. Soc.*, 1930, **52**, 2198; J. W. McBain, D. N. Jackman, A. M. Bakr, and H. G. Smith, *J. Phys. Chem.*, 1930, **34**, 1439; J. W. McBain, H. P. Lucas and P. F. Chapman, *J. Am. Chem. Soc.*, 1930, **52**, 2668.

writer to conclude that the true form of the sorption isotherm in the absence of competing impurity would be of a very different type. Most of the sorption would then take place at minute relative humidities, thereafter increasing to only minor extent with increase of pressure. Such results are

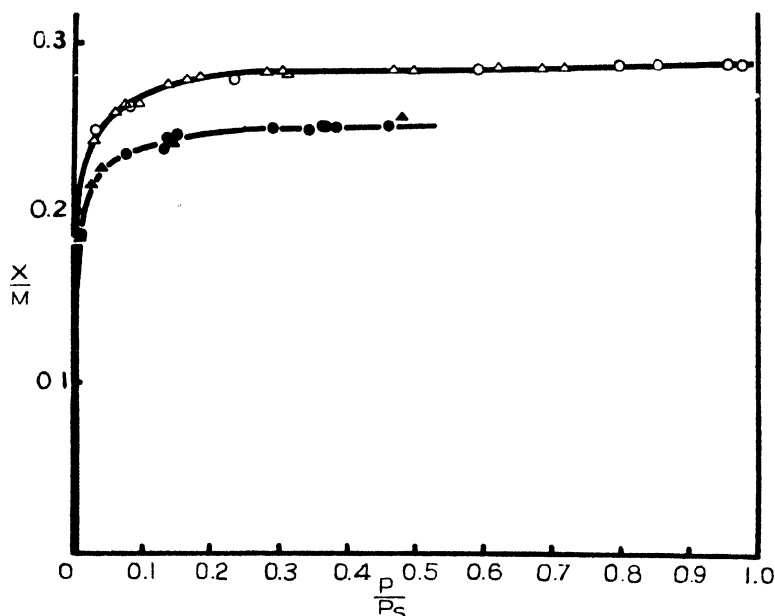


Fig. 45.—Isotherms for the Sorption of Octane by Air-Activated Sugar Charcoal. ○ and △—120°; ● and ▲—205°.

illustrated by figs. 44,¹ 45,² 46,³ and 47,⁴ all referring to activated sugar charcoal, although activated by different methods.

¹ J. W. McBain, H. P. Lucas, and P. F. Chapman, *J. Am. Chem. Soc.*, 1930, **52**, 2676, fig. 3.

² J. W. McBain, H. P. Lucas, and P. F. Chapman, *J. Am. Chem. Soc.*, 1930, **52**, 2678, fig. 6.

³ J. W. McBain, D. N. Jackman, A. M. Bakr, and H. G. Smith, *J. Phys. Chem.*, 1930, **34**, 1444, fig. 2.

⁴ J. W. McBain, D. N. Jackman, A. M. Bakr, and H. G. Smith, *J. Phys. Chem.*, 1930, **34**, 1444, fig. 3.

It is very interesting that the saturated hydrocarbons, like the aromatic hydrocarbons, exhibit sorption which goes to completion at very low pressures, whereas methyl alcohol ¹ is imperfectly sorbed at low pressures, its sorption depending very greatly upon the actual value of the pressure. It might have been thought ² that the first type of sorption was that

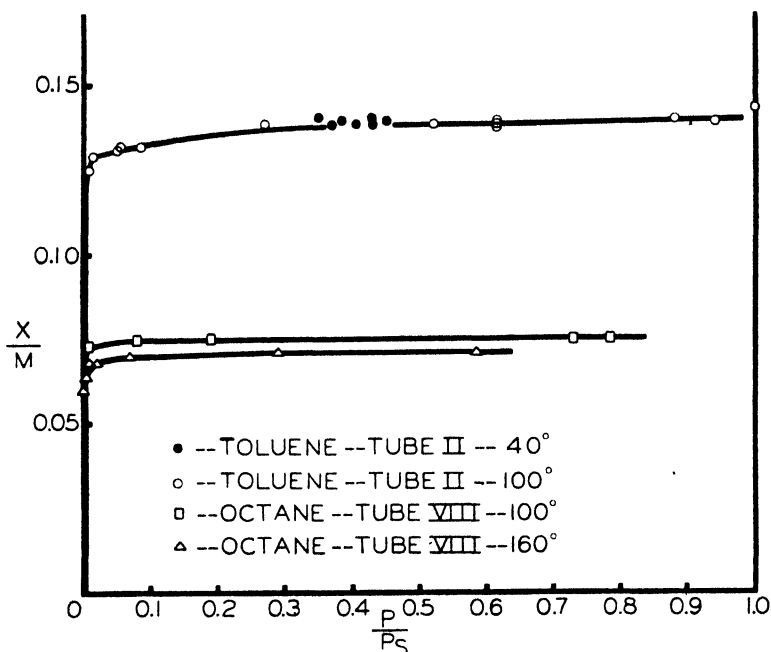


Fig. 46.—Isotherms for the Sorption of Toluene and of Octane by Air-Activated Sugar Charcoal.

for non-polar compounds and the second that of polar molecules. However, this is not borne out by the fact that the sorption of acetone, whose permanent dipole moment is 2.7×10^{-18} , closely resembles that of the hydrocarbons whose

¹ J. W. McBain, H. P. Lucas and P. F. Chapman, *J. Am. Chem. Soc.*, 1930, **52**, 2668; J. W. McBain, D. N. Jackman, A. M. Bakr, and H. G. Smith, *J. Phys. Chem.*, 1930, **34**, 1439; E. Berl and K. Andress, *Z. angew. Chem.*, 1921, **34**, 381.

² A. S. Coolidge, *J. Am. Chem. Soc.*, 1927, **49**, 708.

dipole moment is 0.0×10^{-18} ; whilst methyl alcohol, the other extreme, has a dipole moment of the intermediate value 1.7×10^{-18} . Possibly with ideal cleansing of the charcoal, even methyl alcohol would conform to the "rectangular" type of sorption curve.

Coolidge's isotherms for benzene are shown in fig. 48,¹

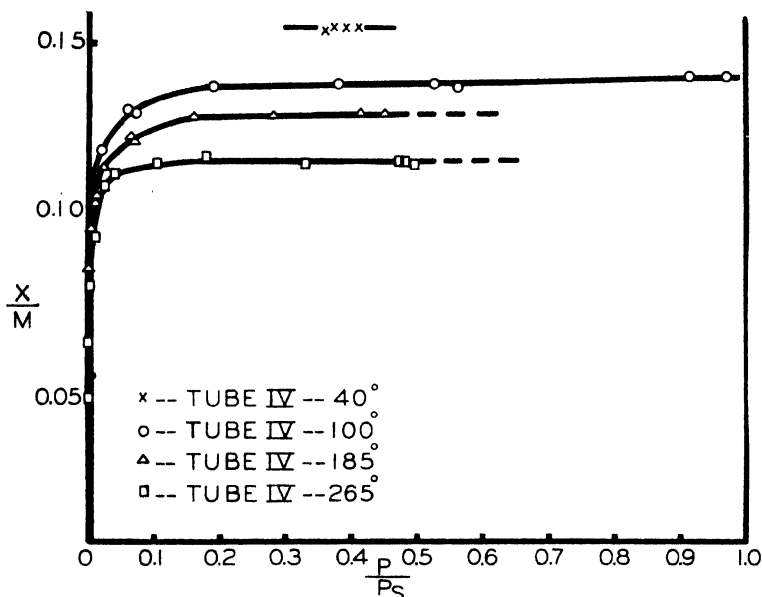


Fig. 47.—Isotherms for the Sorption of Benzene by Air-Activated Sugar Charcoal.

giving the number of cubic centimetres (probably at N.T.P.) sorbed per gram of activated coconut charcoal. He prefers the representation given in fig. 49.² Coolidge's isosteres are linear when plotted as in fig. 50³ which shows that the logar-

¹ A. S. Coolidge, *J. Am. Chem. Soc.*, 1924, **46**, 610, fig. 3.

² A. S. Coolidge, *J. Am. Chem. Soc.*, 1924, **46**, 612, fig. 4.

³ A. S. Coolidge, *J. Am. Chem. Soc.*, 1924, **46**, 613, fig. 6. The isosteres of J. N. Pearce and H. F. Johnstone (*J. Phys. Chem.*, 1930, **34**, 1270) are similar; since they are linear and parallel, the heats of adsorption change but little either with temperature or with amount of sorption.

ithm of the pressures for a constant amount of sorption at various temperatures changes linearly with the reciprocal of the absolute temperature. This is like the vapour pressure curve of an ordinary liquid, but the slope in one case corresponds to the heat of sorption and in the other to the heat of vaporization of the liquid. The value of the exponent n in the ordinary sorption equation applied to Coolidge's results with benzene, for example, varies from about 20 at low tem-

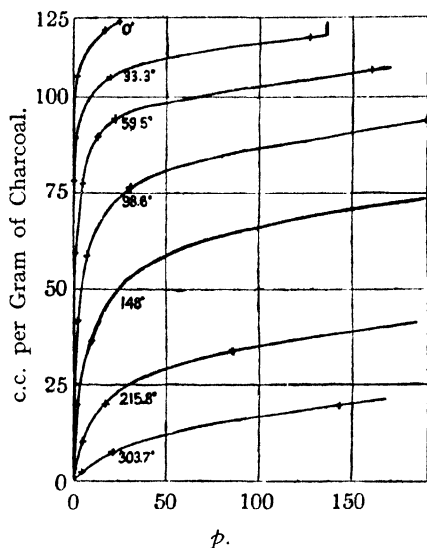


Fig. 48.—Coolidge's Isotherms for the Sorption of Benzene by Charcoal.

peratures and high concentrations to unity at high temperatures and low concentrations. The results obtained by the writer and his collaborators do not fit this equation at all, since at low concentrations n approaches unity and at higher relative pressures, where the sorption is nearly independent of the pressure, the value of n becomes enormous.

Chaplin's curves for sorption of carbon tetrachloride by four kinds of activated gas-mask charcoal, all of 10–12 mesh, are shown in fig. 51.¹

The interpretation of the results obtained with high vacuum technique and the sorption balance as being more nearly typical of the sorption of pure vapours than other published

¹ R. Chaplin, *Proc. Roy. Soc. (London)*, A, 1928, **121**, 344; A. J. Allmand and J. E. Manning, *J. Soc. Chem. Ind.*, 1928, **47**, 372T, fig. 6; A. J. Allmand and R. Chaplin, *Proc. Roy. Soc. (London)*, A, 1930, **129**, 235, 252; L. J. Burrage, *J. Phys. Chem.*, 1930, **34**, 2210; A. J. Allmand and A. Puttick, *Proc. Roy. Soc. (London)*, A, 1930, **130**, 197.

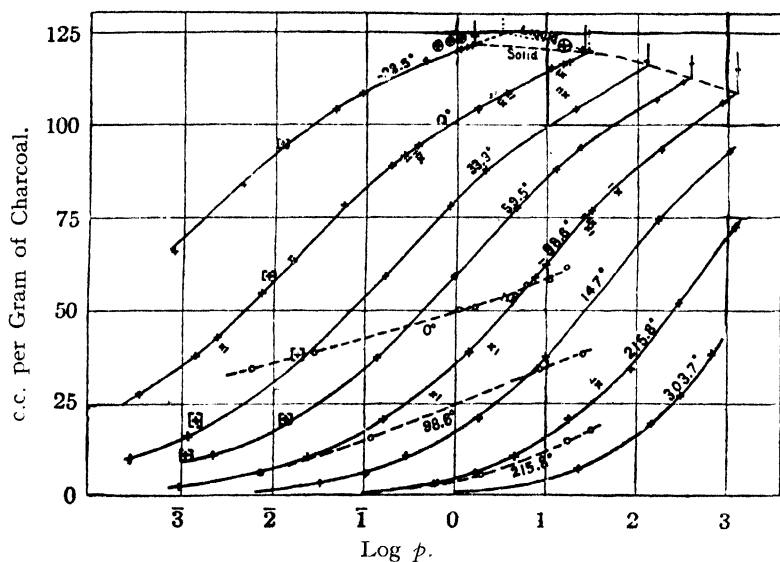


Fig. 49.—Coolidge's Semi-log Isotherms for the Sorption of Benzene by Charcoal.

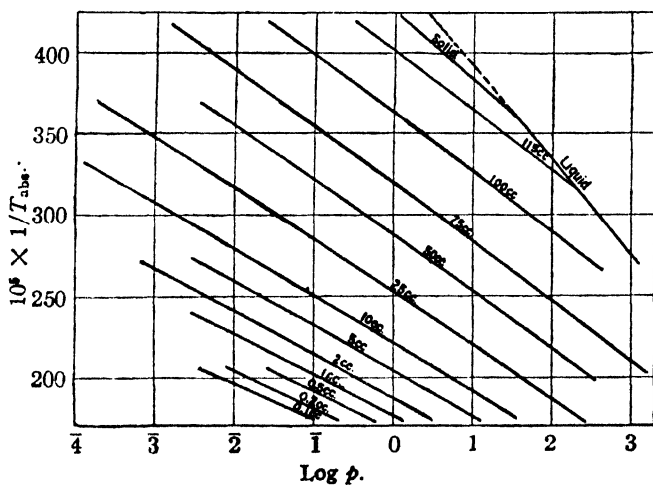


Fig. 50.—Coolidge's Isosteres for the Sorption of Benzene by Charcoal

work,¹ is borne out by the fact that results obtained by a dynamic method in the presence of air are wholly different in that they conform to the ordinary isotherm.² It is evident that the imperfect sorption at low pressures is due to the competition of the impurities, here in particular the air present.

A further argument is that sorption is quick, and final equilibrium is attained almost at once when impurities are

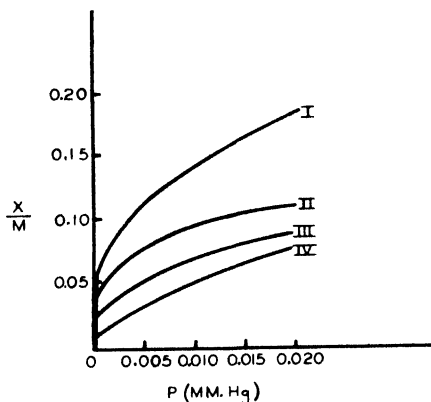


Fig. 51.—Isotherms for the Sorption of Carbon Tetrachloride in Grams per Gram of Charcoal.

- I.—American steam-activated coconut charcoal.
- II.—British steam-activated mixed nut charcoal.
- III.—British air-activated birchwood charcoal.
- IV.—German zinc chloride activated pinewood charcoal.

largely removed. R. F. Sessions in the writer's laboratory has obtained the only information available as to the effects of very long periods of time (three to four years). Using the

¹ The extensive experiments of B. Gustaver (*Kolloidchem. Beihefte*, 1921, **15**, 271–306) with alcohol and acetic acid are not quoted here on account of the complicated hysteresis effects which were probably due to faulty vacuum technique; B. Gustafson, *Arkiv. Kemi Mineral. Geol.*, 1919, **7**, No. 22, 1.

² E. Berl and K. Andress, *Z. angew. Chem.*, 1921, **34**, 377; (ether, ethyl alcohol, methyl alcohol, benzene, carbon tetrachloride, acetone at 0°, 20°, 50° and 100° by zinc chloride activated charcoal). E. Berl and E. Wachendorff, *Z. angew. Chem.*, 1924, **37**, 747; (benzene).

sorption balance, he found that sorption by drastically evacuated charcoal is appreciably complete within about a week and thereafter remains constant year after year.

For comparison of the relative amounts of various vapours taken up under similar conditions by the same charcoal, R. F. Sessions has collected for the first time and calculated in terms of x/m by weight the extensive results obtained by Hunter¹ in Fontana experiments. The recalculated data are given in table 26.

Baerwald² found that at one atmosphere pressure pith charcoal sorbs about 300 volumes and coconut meat charcoal about 240 volumes of any vapour, provided that the charcoal is at the boiling point of the liquid in question, the volume of the charcoal being calculated by its specific gravity in water.

See Chapter III, page 42, for the identical result obtained by Dewar for hydrogen, nitrogen, oxygen and probably helium.

A more quantitative comparison of the sorption of various vapours by one gram of a given charcoal is afforded by the results of Coolidge³ as illustrated in table 27. He gives a long list of factors influencing the sorption obtained.

The most enlightening comparison is that displayed in the following table 28 which embraces the results obtained by Coolidge and by Goldmann and Polányi at 0° C. for relative humidities approaching the saturation value. In table 21 it is seen that the number of grams of various vapours sorbed by the same charcoal is by no means the same; neither is the number of molecules nor their area if the molecules are assumed to be spheres. However, a surprisingly simple rule emerges, first pointed out by Gurwitsch⁴; namely, that approximately equal volumes of all liquids are sorbed.

¹ J. Hunter, *J. Chem. Soc.*, 1865, **18**, 285; 1867, **20**, 160; 1886, **21**, 186; 1871, **24**, 76; 1872, **25**, 649.

² H. Baerwald, *Ann. der Physik* (4), 1907, **23**, 84.

³ A. S. Coolidge, *J. Am. Chem. Soc.*, 1924, **46**, 596.

⁴ L. G. Gurwitsch, *J. Russ. Phys.-Chem. Soc.*, 1915, **47**, 805; *Z. physik. Chem.*, 1914, **87**, 323. On the other hand, he found that the heat effect for these equal volumes was very different and was parallel with chemical reactivity. See Chapter XIV, page 410.

TABLE 26

*Sorption Values, x/m, observed by Hunter for various Vapours at 600 to 700 mm. Pressure, using Coconut Charcoal**

Substance	100° C.	125°-129° C.	155°-159° C.	191°-198° C.
Hydride of benzoyl †	—	—	—	0·25
Aniline . . .	—	—	—	0·24
Butyric ether . . .	—	—	—	0·24
Carbolic acid . . .	—	—	—	0·23
Naphthaline . . .	—	—	—	0·23 ‡
Oxalic ether . . .	—	—	—	0·19
Butyric acid . . .	—	—	—	0·17
Acetic ether . . .	0·35	—	0·19	—
Oil of turpentine . . .	—	—	—	0·16
Bisulphide of carbon . . .	0·31	—	0·20	0·15
Acetic acid . . .	—	—	0·16	—
Salicylic acid . . .	—	—	—	0·13 ‡
Nitrobenzol . . .	—	—	—	0·12 ‡
Hydride of salicyl . . .	—	—	—	0·11
Triethylamine . . .	—	—	—	0·09 §
Acetate of methyl . . .	0·25	—	—	—
Alcohol . . .	0·21	0·16	0·13	0·08
Ether . . .	0·21	0·16	0·12	—
Camphor . . .	—	—	—	0·08 ‡
" Aldehyde " ¶	0·21	—	0·09	—
Iodide of ethyl . . .	0·20	—	—	—
Acetone . . .	0·20	—	0·12	0·07
Ethylamine . . .	0·20	—	0·12 **	0·06 §
Valerianic acid . . .	—	—	—	0·06
Fousel oil . . .	—	—	0·08	—
Iodide of amyl . . .	—	—	0·07	—
Benzol . . .	—	0·14	—	—
Methylic alcohol . . .	0·17 ††	0·13	0·06	0·04
Nitrous ether . . .	0·16	—	—	—
Hydrochloric ether . . .	0·15	—	—	—
Formic acid . . .	—	—	0·04	—
Chloroform . . .	0·12	—	0·07	—
Amylene . . .	—	—	0·03	—
Hexachlorethane . . .	0·07	—	0·02	—
Water . . .	—	0·02	0·013	—
Carbonic anhydride (0·16) ††	—	0·02	—	—
Cyanogen (0·28) §§	0·08	—	—	—
Ammonia (0·15) §§	(0·06)	0·013	—	—

* R. A. Smith (*Chem. News*, 1868, **18**, 121 ; 1879, **39**, 77 ; *Proc. Roy. Soc. (London)*, 1879, **28**, 322) found that charcoal which took up one volume of hydrogen sorbed 7·99 volumes of oxygen, 6·03 of carbon monoxide, 22·05 of carbon dioxide, 10·01 of marsh gas, 12·90 of nitrous oxide, 36·95 of sulphur dioxide, 7·06 of air, and 4·27 of nitrogen.

† Benzaldehyde. ‡ At 226° to 230° C. § At 182° to 189° C.

|| 0·23 at 90° C. ¶ Assumed formaldehyde.

** At 142° to 151° C. †† 0·18 at 91° C.

‡‡ At room temperature. By increase of pressure this was increased by as much as tenfold. §§ At room temperature. |||| At 70° C.

TABLE 27

*Coolidge's Data for the Sorption of various Vapours by Activated * Coconut Charcoal*

Substance	p/p_s for $x/m = 100$ c.c. vapour sorbed		x/m in c.c. vapour for $p/p_s = 1$	
	at 0° C.	at 60° C.	at 0° C.	at 60° C.
Benzene	0.030	0.129	120.3	112.7
Ether	0.16	0.87	109.5	100.7
Carbon disulphide	0.0074	0.0269	171.1	160.0
Methanol	0.025	0.085 †	255.5	236.0
Chloroform	0.023	0.219 †	126.7	—
Carbon tetrachloride	—	—	103.5	—
Ethyl formate	0.022	0.214 †	130.0	—
Methyl acetate	0.010	0.098 †	142.5	—
Water	0.30	0.38 †	528	511

* The higher the temperature of evacuation, the greater the sorption for low relative pressure, but the less the ultimate sorption when the relative humidity approached saturation. Inactive charcoal evacuated at 550° C. was a slightly better sorbent than the corresponding active charcoal at low relative pressures, but far less efficient at high relative pressures. In experiments at too high a temperature decomposition is observed except for benzene, above 300° C. with ether and carbon disulphide, and even at 100° C. with all the others.

† At 100° C.

Langmuir ¹ had thought that this must be due to the pores becoming completely filled with condensed liquid in addition to that which is sorbed, but the present data indicate that it is nearly true of the sorbed liquid itself.

Lamb and Coolidge ² found a similar result with nine organic vapours, and pointed out that it held for Titoff's experiments for ammonia and carbon dioxide. They did not make the statement in this form but pointed out the inverse proportionality between cubic centimetres of gas or number of mols sorbed and molar volume. Since 1 c.c. of each of their liquids exhibited the same net heat of sorption for transfer from the liquid state to the charcoal, this likewise involves inverse proportionality between the amount of sorption and net heat of sorption.

¹ I. Langmuir, *J. Am. Chem. Soc.*, 1917, **39**, 1903.

² A. B. Lamb and A. S. Coolidge, *J. Am. Chem. Soc.*, 1920, **42**, 1166.

TABLE 28

Data of Coolidge and of Goldmann and Polányi, showing the Amounts of various Vapours sorbed by One Gram of Charcoal at 0° when the Relative Pressure, p/p., is approaching Unity.*

Substance	x/m in grams	x/m in mols	Area † (spherical x/m in molecules)	x/m in c.c. of liquid
Goldmann and Polányi				
Ethyl chloride	4.98	0.0773	1.32	5.40
Ethyl ether	3.96	0.0534	1.16	5.38
Normal pentane	3.46	0.0480	1.12	5.38
Carbon disulphide . . .	7.02	0.0923	1.40	5.42
Coolidge				
Ethyl ether	3.62	0.0488	1.06	4.90
Carbon disulphide . . .	5.81	0.0764	1.16	4.50
Ethyl formate	4.30	0.0580	1.06	4.54
Methyl acetate	4.70	0.0634	1.16	4.90
Chloroform	6.74	0.0564	1.04	4.42
Carbon tetrachloride . .	7.10	0.0461	0.96	4.35
Methyl alcohol	3.65	0.1139	1.32	4.50
Water	4.24	0.2358	1.62	4.24

* F. Goldmann and M. Polányi, *Z. physik. Chem.*, 1928, **132**, 356, Table 17. G. C. Schmidt and B. Hinteler (*Z. physik. Chem.*, 1916, **91**, 120) in experiments where evacuation was only carried to 0.04 mm. found a fairly large variation in the volumes sorbed by animal charcoal, using benzene, hexane, carbon disulphide, chloroform, acetone, ethyl alcohol and methyl alcohol (and water).

† "Area" = $\frac{x}{mM} \left(\frac{M}{d} \right)^{\frac{2}{3}}$ where M is the molar weight and d is the density of the liquid. J. Traube and St. Birutowitsch (*Kolloid-Z.*, 1928, **44**, 233) found that when air saturated by various vapours was brought into contact with activated charcoal and silica gel, the product of the number of sorbed molecules by the surface of one molecule as calculated from the molar refraction was approximately constant, which they took as confirmation of the theory of Langmuir. Their experiments were made with water, carbon disulphide, methyl acetate, acetone, methyl alcohol, hexane, ethyl acetate, ethyl alcohol, benzene, methyl ethyl ketone, propyl alcohol and iso-amyl alcohol by charcoal; and methyl acetate, acetone, benzene and methyl ethyl ketone by silica gel. E. V. Alekseevski (*J. Russ. Phys.-Chem. Soc.*, 1924, **55**, 401) likewise investigated by a dynamic method the sorption of saturated vapours of 72 organic compounds and of bromine and of water by animal charcoal. x/m attained the unlikely values of 0.706 for water, 0.741 for benzene, 0.364 for bromine, and 3.724 for $C_6H_{11}ONO$, etc. etc.

Tryhorn and Wyatt¹ found that substantially the same values of x/m as obtained with a saturated vapour of benzene were obtained by the simple expedient of soaking the charcoal in liquid benzene and weighing it at the moment when the visible liquid surface had just disappeared through evaporation. Cude and Hulett² with a similar procedure or, better, by centrifuging in a Gooch crucible obtained results constant to 2 per cent. However, further tests are necessary to remove ambiguity due to possible bulk condensation because in neither case were these results compared with the values obtained from slightly unsaturated vapours.

Driver and Firth,³ who exposed animal charcoal to saturated vapours until approximately constant amounts were sorbed (from 61 hours for carbon tetrachloride up to 205 days for methyl benzoate), found that the volumes so obtained varied from 0.417 c.c. toluene up to 0.684 c.c. carbon disulphide per gram of that charcoal. Results that were fully as divergent were obtained with five other charcoals. They therefore question the conclusion of Gurwitsch. However, this does not by any means invalidate the regularity found in such work as that of Coolidge and of Goldmann and Polányi in table 21 where the vapours were not quite saturated and condensation was definitely controlled, instead of, as here, being left to chance. Furthermore, Driver and Firth's charcoals were exposed to air after evacuation.

It is interesting that the results obtained by the writer and his collaborators for the members of the normal straight chain hydrocarbons from pentane to decane show that approximately equal weights and therefore approximately equal volumes of each of these are sorbed by a given charcoal.

¹ F. G. Tryhorn and W. F. Wyatt, *Trans. Farad. Soc.*, 1926, **22**, 134. Their data for the maximum sorption they observed in the presence of saturated vapours indicated that different volumes of the different liquids are sorbed by the charcoal, ranging from 0.13 c.c. for water and butyl alcohol up to 0.19 c.c. per gram of charcoal for ether and acetone. (They mention 0.16 to 0.18 c.c.)

² H. E. Cude and G. A. Hulett, *J. Am. Chem. Soc.*, 1920, **42**, 398, footnote 1.

³ J. Driver and J. B. Firth, *J. Chem. Soc.*, 1922, **121**, 2409.

independent of the length of the paraffin chain and therefore independent of the number of individual molecules.

Comparing the results obtained by McBain and his collaborators with each other,

"Bakr and McBain¹ observed that with Kahlbaum's (un-activated) sugar charcoal and their particular technique the weight of acetic acid which could be sorbed by one gram of charcoal was 1.34 times greater than the weight of toluene which could be sorbed under the same conditions. It is interesting to note that in the experiments here recorded for activated sugar charcoals, 'Air C', Wright's 'Steam D', and 'Air and Vacuum B', the corresponding ratios for acetic acid and toluene are 1.35, 1.35 and 1.36 respectively. Such comparisons can only be made when the vacuum technique for both cases is precisely similar. Likewise, in the present experiments, the relative maximum amounts which can be sorbed by 'Air and Vacuum B', Wright's 'Steam D', and 'Air C' charcoals are in the proportion of 1 to 1.04 and 2.38, respectively, for acetic acid and 1 to 1.03 and 2.37 respectively, for toluene. Activation thus exerts similar effects upon the sorption of both substances."²

However, this does not exactly agree with equal volumes of toluene and acetic acid. The volume of acetic acid, instead of being equal to that of toluene, is 1.117 times greater, taking the densities of the free liquids at 120° C. Since the two liquids are equally compressible, the only suggestion for explaining the difference is that the influence of the size and shape of the molecule is affecting the amount of close packing possible in the nearly rigid ultra-pores of the charcoal.

Others who have studied sorption of vapours by various charcoals include Urbain,³ Pearce and Knudson,⁴ Hällström,⁵

¹ A. M. Bakr and J. W. McBain, *J. Am. Chem. Soc.*, 1924, **46**, 2718.

² J. W. McBain, H. P. Lucas, and P. F. Chapman, *J. Am. Chem. Soc.*, 1930, **52**, 2678.

³ E. Urbain, *Compt. rend.*, 1925, **180**, 63. (Benzene, chlorine and chloropicrin.)

⁴ J. N. Pearce and C. M. Knudson, *Proc. Iowa Acad. Sci.*, 1927, **34**, 197. (Methyl alcohol, ethyl alcohol, water, ammonia and methylamine by ash-free coconut charcoal.) See also C. M. Knudson, *Dissert.*, State University of Iowa, 1924.

⁵ M. af Hällström, *Dissert.*, Helsingfors, 1920. (Some results reproduced by B. Gustaver, *Kolloidchem. Beihefte*, 1921, **15**, 331.)

Bunbury,¹ and Clemente.² As regards the influence of temperature upon the decrease of sorption with rise of temperature for relative humidity approaching saturation, Coolidge³ pointed out that as a first approximation the charcoal behaves like a vessel of constant capacity, whereas the sorbed vapour expands almost as much as the free liquid. Goldmann and Polányi found (except for carbon disulphide) that the expansion of the sorbed material was between 17.6 and 24.8 per cent less than that of a corresponding weight of ordinary free liquid.

The writer has long been troubled with the curious difficulty which arises in attempting to apply the equation for calculating heat of sorption from the effect of temperature (see Chapter XIV, page 400) in the cases where the isotherms show saturation values or approach saturation values. In ordinary cases of sorption one may construct an isostere, that is, a curve for the pressures required to produce the same sorption at different temperatures. However, this is a physical impossibility when the saturation values are different at different temperatures and an amount of sorption within the range of these saturation values is under discussion. Neither the thermodynamic equation nor its derivation provides for this contingency. This breakdown of the formula throws suspicion upon results obtained from data which are in the neighbourhood of a saturation value and must affect to a certain degree all data obtained from such systems. The formula applies once more, quite strictly, when the saturation pressure is just exceeded and liquid is being condensed. It then gives heat of vaporization of the liquid. There is a complete hiatus between these results and those obtained from amounts of sorption which at the higher temperature are less than the saturation value of sorption at the lower temperature.

¹ H. M. Bunbury, *J. Chem. Soc.*, 1922, **121**, 1525. (Carbonyl chloride.)

² A. Clemente, *Dissert.*, Chicago, 1924 (benzene and ethyl alcohol by coconut charcoal at 20° C.) An equal number of molecules were sorbed at saturation.

³ A. S. Coolidge, *J. Am. Chem. Soc.*, 1926, **48**, 1812, table 2.

The writer's point of view in elucidation of this paradox is as follows. The thermodynamic formula assumes that the equilibria at two temperatures are identical in nature and that the solid phase has the same composition at both temperatures, differing only in temperature, and in the external equilibrium gaseous pressure to which it is submitted. The writer suggests that these conditions are not fulfilled in the case of sorption at different temperatures, more especially in the region of saturation. He considers that the solid is in a state of strain which has to be taken into account before the heat of sorption may be calculated with exactitude. Sorption resembles systems in which one of the phases is under pressure or is being squeezed. It is well known that the vapour pressure or solubility or dissociation pressure of a solid is increased if the solid only is subjected to pressure or is being squeezed or strained. This would appear to be the case in sorption of vapours by charcoal.

We have just seen that sorbed vapours exhibit isotherms which approach or practically attain saturation values, and that these saturation values diminish with rise of temperature rather less than would correspond to the expansion in volume which would be exhibited by the same amount of liquid. It is shown in Chapter XIII that the charcoal is expanded by the sorbed vapour, slightly but unmistakably. Nevertheless, unlike gelatin, which swells and finally dissolves in water, or similarly, rubber in benzene, the charcoal retains its coherence. Hence it seems altogether probable that the structure of the charcoal is resisting the penetration of the vapour molecules and their attempt to cover all the exposed valencies of the atoms of the solid. It seems further probable that, owing to increase of thermal vibration with temperature, the higher the temperature the greater the squeezing effect upon the close packed molecules of sorbed material and hence the greater the strain upon the structure of the charcoal.

The writer's hypothesis of steric hindrance and its implications for temperature coefficient and heat of sorption as outlined in the foregoing paragraphs would seem to apply in

some degree to most cases of sorption, its consequences becoming negligible only at very low values of sorption.

Summary.—When we consider that all gases become vapours below their respective critical temperatures, we see how far-reaching a concise description of the behaviour of vapours can be. We therefore summarize the regularities observed with vapours in the following five rules:

Rule 1.—Sorption is related to condensibility in one or other of the ways already enumerated in Chapter III, page 54. This means an enormous difference in practice between such substances as helium on the one extreme and the vapour of a high-boiling liquid on the other.

Rule 2.—At all temperatures the amount of sorption depends primarily upon the relative pressure, p/p_s . Goldmann and Polányi prefer the expression $RT \ln p_s/p$, but this is equally approximate.

Rule 3.—With thoroughly evacuated charcoal the sorption is still large (30–50 per cent of its largest value) when the pressure is infinitesimal, as for example, benzene at liquid air temperature exposed to charcoal at 100 or 200° C.

Rule 4.—Equal volumes of different vapours, measured in the form of the corresponding liquids, are sorbed by a given charcoal when p is approaching p_s .

Rule 5.—The effect of temperature upon the amount of sorption for a given value of p/p_s is to diminish the amount by somewhat less than that corresponding to an expansion of an equal weight of the free liquid. This holds as a first approximation even for low arbitrary values of p/p_s or of $RT \ln p_s/p$.

SORPTION OF WATER

The behaviour of charcoal towards water vapour has frequently presented anomalies hardly paralleled by any other vapour. It appears, on the one hand, as though water vapour were sorbed with difficulty by charcoal in the presence of other competing substances such as the impurities, hydrocarbons and especially oxides which are almost invariably

present.¹ On the other hand, charcoal holds tenaciously some of the small amounts of water sorbed at low pressures, evolving appreciable quantities of water on heating,² and it freely sorbs water vapour at high relative humidity.³

Violette⁴ found that the amount of moisture taken up by wood charcoal from air depended upon the temperature of carbonization of the charcoal, being 21 per cent for 150° C., 7 per cent for 250° C., 6 per cent for 350° C., 4 per cent for 430° C., and down to 2 per cent for 1,500° C., powders sorbing twice as much as lumps. Scheringa's⁵ charcoal obtained from xylene took up about 7 per cent. Tryhorn and Wyatt's⁶ coconut charcoal took up 13 per cent.

The sorption of water by charcoal has been given special attention by Coolidge⁷ and by Allmand and his collaborators.⁸

¹ P. Ehrenberg and K. Schultze (*Kolloid-Z.*, 1914, **15**, 183) showed that the inability to wet very dry powdered soil and lampblack was not due to a covering of fat or wax but was ascribable to sorbed air.

² For example, E. Berl and K. Address (*Z. angew. Chem.*, 1921, **34**, 369) found that zinc chloride activated charcoal gave off 15.3 per cent of water in an atmosphere of nitrogen at 110° to 150° C.; on standing at room temperature for six hours it had re-absorbed 3 per cent of moisture. H. Isobe (*Eng. Chem. J.* (Japan), 1921, **1**, 99) found that various wood, nut and bone charcoals, dried at 150° C., took up from 8–20 per cent by weight from air saturated with moisture. See also B. E. Brown, *Phys. Rev.* (2), 1921, **17**, 700.

³ J. Driver and J. B. Firth (*J. Chem. Soc.*, 1922, **121**, 2412) found that the amounts taken up from saturated water vapour by various charcoals varied from 5 to 38 per cent by weight; W. B. Wiegand and C. R. Boggs (*Ind. Eng. Chem.*, 1930, **22**, 823) found from 4 to 56 per cent for different carbon blacks.

⁴ H. Violette, *Compt. rend.*, 1853, **36**, 850.

⁵ K. Scheringa, *Pharm. Weekblad*, 1921, **58**, 937.

⁶ F. G. Tryhorn and W. F. Wyatt, *Trans. Farad. Soc.*, 1926, **22**, 134.

⁷ A. S. Coolidge, *J. Am. Chem. Soc.*, 1924, **46**, 623; 1927, **49**, 708.

⁸ P. G. T. Hand and D. O. Shiels, *J. Phys. Chem.*, 1928, **32**, 441; A. J. Allmand, R. Chaplin and D. O. Shiels, *J. Phys. Chem.*, 1929, **33**, 1151; A. J. Allmand and P. G. T. Hand, *J. Phys. Chem.*, 1929, **33**, 1161; A. J. Allmand, P. G. T. Hand, J. E. Manning, and D. O. Shiels, *J. Phys. Chem.*, 1929, **33**, 1682; A. J. Allmand, P. G. T. Hand, and J. E. Manning, *J. Phys. Chem.*, 1929, **33**, 1694; L. J. Burrage, *J. Phys. Chem.*, 1930, **34**, 2211.

Two of Coolidge's diagrams are reproduced in figs. 52 and 53.¹ Fig. 52 is especially striking because it compares the typical behaviour of the sorption of water by very different types of porous bodies and surfaces. The two central curves on the diagram represent the sorption of water vapour by ash-free

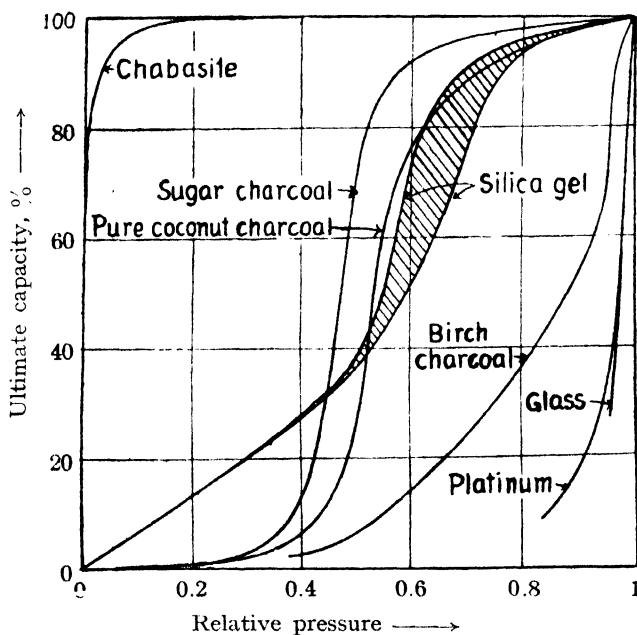


Fig. 52.—Sorption of Water Vapour by Various Materials expressed in percentage of the Maximum Values observed in each Case.

steam-activated sugar charcoal and by activated coconut charcoal previously extracted with hydrofluoric acid. It is seen that not more than 1 per cent of the total water has been taken up when the relative pressure is as high as one-third and that most of it has been taken up when the relative

¹ A. S. Coolidge, *J. Am. Chem. Soc.*, 1927, **49**, 712, fig. 3, and 716, fig. 4.

pressure $p/p_s = \frac{2}{3}$. The other curves in fig. 52 are quoted from other workers.¹

It will be seen in fig. 52 that chabasite exhibits an almost rectangular form of isotherm which has been suggested by the writer as ideal for the persorption of vapours by charcoal. Most of the persorption occurs at infinitesimal pressures. The presence of ash in charcoal greatly increases the amount of

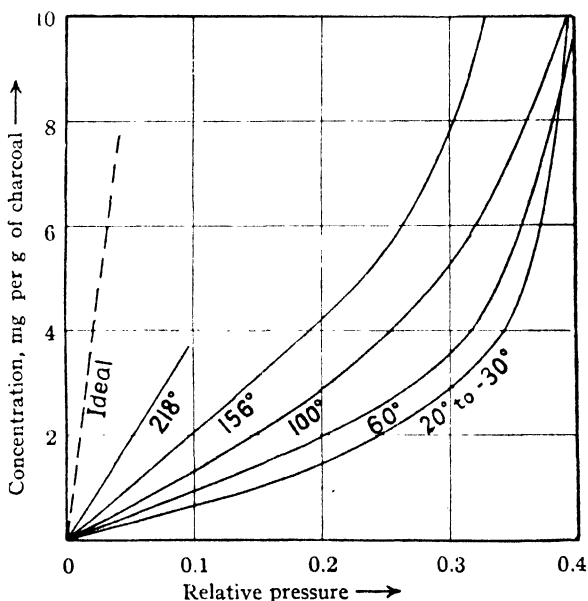


Fig. 53.—Initial Portions of the Isotherms for the Sorption of Water Vapour by Sugar Charcoal (Coolidge).

water taken up at very low pressures, and some of it is irreversibly retained.²

¹ For chabasite, unpublished results from the Harvard laboratory by J. C. Woodhouse; for birchwood charcoal, H. H. Lowry and G. A. Hulett, *J. Am. Chem. Soc.*, 1920, **42**, 1393; for silica gel, J. S. Anderson, *Z. physik. Chem.*, 1914, **88**, 191; for platinum and glass, I. R. McHaffie and S. Lenher, *J. Chem. Soc.*, 1925, **127**, 1559.

² Compare A. S. Coolidge, *J. Am. Chem. Soc.*, 1924, **46**, 625. However, N. K. Chaney, A. B. Ray, and A. St. John (*Ind. Eng. Chem.*, 1923, **15**, 1248) state that water is "practically completely removed"

Fig. 53 is a detailed study of the sorption by the ash-free sugar charcoal at low relative pressures and at temperatures from -30°C. to 218°C. The dashed curve marked "ideal" connects the origin with the value for $p/p_s = 1$. The usual hysteresis has been almost eliminated in these careful experiments except that in desorption at the lowest pressures it was necessary to heat the charcoal with or without liberation of the water in order to re-attain equilibrium. Henry's law of direct proportionality between sorption and pressure holds below relative pressures of 0.1. The isotherms from $+20^{\circ}$ to -30°C. are indistinguishable, which shows that the heat of sorption is exactly the same as the heat of vaporization of liquid water.¹ The greater sorption at higher temperatures showed that the heat of sorption is less than the heat of vaporization of water, the first such case to be discovered. Another point of interest is that the saturation capacity of charcoal for water is at a maximum at 0°C.

Almost every investigator interprets the curves for water as indicating capillary condensation in the larger pores (compare Chapter XVI) and has regarded adsorption as being negligible. Coolidge suggests that the sorbed water at very low pressures is in single molecules and at higher pressures is associated like ordinary water.

by the passage of dry air at room temperature. A. V. Rakovsky (*J. Russ. Phys.-Chem. Soc.*, 1917, **49**, 371) states that 2 per cent of the water is irreversibly retained by sugar charcoal; some of it is not entirely expelled even by heating to redness in a current of nitrogen.

¹ T. Okazawa (*Bull. Inst. Phys. Chem. Research* (Tokyo), 1928, **7**, 821; English Ed., **1**, 75), on the other hand, found a far greater heat of sorption; namely, 11,700 cal./mol at 40° and 10,200 cal./mol at 100° for charcoal from *Quercus acuta*. This agrees with the positive sign of the heat of wetting found with bone charcoal (L. Gurwitsch, *Kolloid-Z.*, 1923, **32**, 81; W. D. Harkins and D. T. Ewing, *Proc. Nat. Acad. Sci.*, 1920, **6**, 49) and with animal charcoal (J. R. Katz, *Proc. Acad. Sci. Amsterdam*, 1923, **26**, 548) and even with animal charcoal freed from ash (H. Gaudechon, *Compt. rend.*, 1913, **157**, 209); on the other hand, the initial heat of sorption found at 0°C. by F. G. Keyes and M. J. Marshall (*J. Am. Chem. Soc.*, 1927, **49**, 163) with extracted gas-mask charcoal containing 0.36 per cent ash was somewhat less than the heat of condensation, rising rapidly to nearly that value.

In the writer's laboratory R. F. Sessions has shown that with activated sugar charcoal at 120°C . after exceptional evacuation, nearly the whole of the water sorbed is taken up at a relative pressure 0.3. Below this relative pressure sorption is very slight. At this pressure x/m rises to about 40 per cent of the weight of the charcoal. At higher pressures somewhat more water is taken up. Hysteresis was negligible. In experiments with organic vapours such as toluene¹ the same charcoal sorbed at very low pressures a large fraction of the total amount which it was able to take up. However, the final values of x/m for water exceeded those for the organic solvents.

In the first place, the hypothesis of capillary condensation would necessitate the assumption that the pores in the charcoal were all of uniform diameter; that is, equivalent to one long cylinder. It would leave unexplained the characteristic form as well as position of the isotherms for organic vapours whose final x/m values are less, for it would assume that these substances which wet charcoal do not condense, whereas water which wets with difficulty would be condensed, filling a larger volume, the pores being much coarser than molecular dimensions. The writer would reject the hypothesis of capillary condensation and would assume adsorption or, rather, persorption in both cases.

A conclusive argument against the hypothesis that water, in contradistinction to organic substances, is taken up by charcoal through capillary condensation is supplied by experiments of J. L. Porter in the writer's laboratory. He found that charcoal expands when it sorbs organic vapours. Capillary condensation necessitates a tension or negative hydrostatic pressure exerted upon any capillary or pore containing liquid with a concave meniscus, which is the only condition for the existence of liquid below the saturation pressure p_s . Now charcoal, instead of contracting, is found to expand when it takes up water from unsaturated water vapour. This proves that with water as with organic liquids we are dealing

¹ J. W. McBain, H. P. Lucas, and P. F. Chapman, *J. Am. Chem. Soc.*, 1930, **52**, 2676.

with adsorption or persorption, not condensation to liquid in bulk.

Neglecting the slight initial sorption, the question immediately arises as to why water is not sorbed until the relative pressure attains a definite, fairly large value. The only answer is in terms of Langmuir's theory. A molecule of water vapour striking the charcoal surface will evaporate after a very brief interval unless in the meanwhile other molecules have arrived on the adjacent surface. They are then held by mutual polarization and the polarization of the underlying surface which they may effect. The latter polarization will of course disappear almost immediately after evaporation of the water. Sorption will not be complete, that is, it will increase with further increase of relative pressure, because in accordance with the Langmuir theory some spots must be left vacant by evaporation at all pressures below saturation. One is reminded of the much more extreme case of metallic vapours which are not sorbed on glass above a certain critical temperature¹ for a given pressure. These cases are further distinguished by the non-volatility of the metallic vapours at the temperature of the glass. It is probable that search would reveal surfaces and materials ranging from those like charcoal and organic vapours, which exhibit fairly complete sorption at minute relative pressures, through others like water and charcoal, which require moderate relative pressures, to the more extreme cases where greatly super-saturated vapours are required.

The reason that water is sorbed to a greater extent than toluene is obviously on account of the small size of its molecules.

Bartell and Osterhof² from studies of adhesion tension (compare Chapter X, page 345) conclude that "the force of cohesion of benzene molecules for each other is less than the

¹ See I. Langmuir, *Trans. Farad. Soc.*, 1921, **17**, 8; *Phys. Rev.* (2), 1916, **8**, 149; compare J. Chariton and N. Semenov, *Z. Physik*, 1924, **25**, 287; J. Frenkel, *Z. Physik*, 1924, **26**, 117; Chapter XVIII, page 482, footnote 2; also the general discussions in Chapter XVIII.

² F. E. Bartell and H. J. Osterhof, *Colloid Sym. Mon.* (Michigan, 1927), 1928, **5**, 128, 132.

force of adhesion of benzene molecules for carbon. The force of cohesion of water molecules for each other is greater than the force of adhesion of water molecules for carbon," but they calculate that the adsorption pressure of water on charcoal is between 5,600 and 10,900 atmospheres, a greater value than that for organic compounds.

Allmand and his collaborators ¹ have made a most elaborate and extensive study of the sorption of water vapour. They summarize the typical results of earlier workers in fig. 54 ² in which the co-ordinates are reversed as compared with

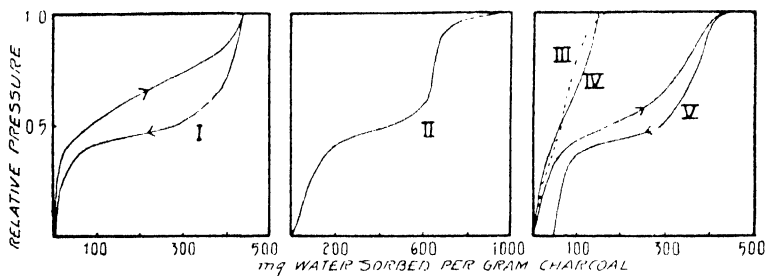


Fig. 54.—Sorption of Water Vapour by Charcoal.

- I.—Berl and Andress. Sorption and desorption curves.
- II.—Katz. Mean of sorption and desorption curves.
- III.—Rakovsky. Coconut charcoal. Sorption curve.
- IV.—Rakovsky. Sugar charcoal. Sorption curve.
- V.—Rakovsky. Blood charcoal. Sorption and desorption curves.

figs. 52 and 53. Here the curves are the same type but with very pronounced hysteresis.

Allmand's charcoals lost the following percentages by weight on heating at 140° C., evacuating at 270° C. and at 800° C., respectively: English air-activated birchwood, 15, 15 and 18 per cent; German pinewood, zinc chloride activated,

¹ See footnote 8, page 144; also for low pressures, A. J. Allmand and R. B. King, *Proc. Roy. Soc. (London)*, A, 1930, **130**, 210.

² A. J. Allmand, R. Chaplin, and D. O. Shiels, *J. Phys. Chem.*, 1929, **33**, 1151, fig. 1; E. Berl and K. Andress, *Z. angew. Chem.*, 1921, **34**, 369; J. R. Katz, *Proc. Acad. Sci. Amsterdam*, 1923, **26**, 548; A. V. Rakovsky, *J. Russ. Phys.-Chem. Soc.*, 1917, **49**, 371.

34 (?), 29 and — per cent ; American steam-activated coconut charcoal, 20, 21 and 24 per cent, respectively.¹ Their experiments on sorption and desorption of water vapour in the presence of air² and nitrogen³ exhibited the usual decided hysteresis, the form of curve depending upon the temperature of previous evacuation. Oxygen, so firmly held by charcoal, had no definite effect on the velocities of sorption and desorption, but it altered the shape of the sorption curves obtained with charcoal evacuated at 800° C.

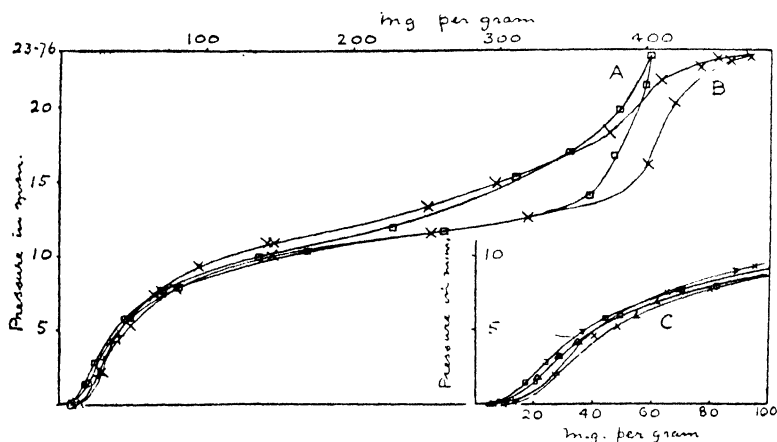


Fig. 55.—Sorption and Desorption of Water Vapour at 25° by American Steam-Activated Coconut Charcoal which has been evacuated, A at 270° and B at 800° C. C shows the curves near the origin on an enlarged scale.

Their most interesting experiments⁴ are those in the absence of gases. Hysteresis is still present as is shown by fig. 55⁵ which shows the effect of temperature of evacuation upon

¹ Compare W. B. Plummer, *Ind. Eng. Chem. Anal. Ed.*, 1930, **2**, 57.

² A. J. Allmand, R. Chaplin, and D. O. Shiels, *J. Phys. Chem.*, 1929, **33**, 1151.

³ A. J. Allmand and P. G. T. Hand, *J. Phys. Chem.*, 1929, **33**, 1161.

⁴ A. J. Allmand, P. G. T. Hand, J. E. Manning, and D. O. Shiels, *J. Phys. Chem.*, 1929, **33**, 1682.

⁵ A. J. Allmand, P. G. T. Hand, J. E. Manning, and D. O. Shiels, *J. Phys. Chem.*, 1929, **33**, 1686, fig. 3.

the position and form of the sorption and desorption curves. Isotherms at 0° , 15° and 25° confirmed the results of Coolidge already discussed, in that they are indistinguishable and that the latent heat of sorption is the same as the latent heat of vaporization.

Extraction of the charcoal with alkali greatly diminishes the sorptive capacity of the charcoal at the lowest pressures, and the quantity of water retained "at zero pressure" is lessened.¹ Allmand, in contradistinction to Coolidge, is convinced that the hysteresis is real and not caused by accumulation in the vapour phase of impurities expelled from the charcoal. He considers it possible² that some of the impurities, such as carbon dioxide, retained in the charcoal, being mobile, may pass from centres of lower to centres of higher sorption potential as the latter are set free during desorption; then on resorption, hysteresis will result if the new material is incapable of displacing the impurities rapidly. Table 29 is a summary of all of Allmand's data by the static method, showing the amounts of water irreversibly retained by the charcoals previously described, page 150, and by activated sugar charcoal. Dynamic experiments give larger values for the water retained. Allmand concludes that it is impossible to account for all of the missing water on the assumption that it has been evolved in the form of water gas but that it is retained even after evacuation at temperatures up to 800°C .

Gustaver's³ numerous measurements with Merck's animal charcoal show rather less hysteresis than in the experiments of Allmand. The initial sorption and desorption appeared reversible, after allowing for water equal to 4 per cent by weight of the charcoal being held even *in vacuo* at room temperature. The maximum weight of water taken up is

¹ A. J. Allmand, P. G. T. Hand, and J. E. Manning, *J. Phys. Chem.*, 1929, **33**, 1694.

² A. J. Allmand and R. Chaplin, *Proc. Roy. Soc. (London)*, A, 1930, **129**, 264.

³ B. Gustaver, *Kolloidchem. Beihefte*, 1921, **15**, 248; B. Gustafson, *Arkiv Kemi Mineral. Geol.*, 1919, **7**, No. 22, 1.

TABLE 29 ¹*Allmand's Experiments on the Imperfect Recovery of Water Sorbed at 25° C. by Charcoal*

Charcoal	Outgassing temperature ° C.	Maximum pressure, mm. Hg	Mg. water per grain of charcoal upon outgassing	
			Recovered	Not recovered
British	270	22.68	3.98	0.30
British	800	6.61	4.48	0.04
British	800	22.10	5.25	2.42
British	800	23.76	6.07	5.99
German	270	23.76	2.91	1.59
German *	270	23.76	2.32	0.00
American	270	23.47	5.09	0.65
American	800	23.44	8.86	1.06
American †	800	23.76	0.01	0.67
Sugar ‡	110	23.25	1.86	3.49
British	800	4.67	7.16	3.56

* Extracted with hydrochloric acid.

† Extracted with alkali.

‡ Extracted with hydrofluoric acid.

$x/m = 0.70$. These figures may be compared to those of Bachmann ² for coconut charcoal with 8 per cent of irreversible water and a maximum x/m of 0.2 to 0.25. Bachmann found two regions of relative pressure exhibiting hysteresis, with reproducible isotherms below, between and above, after the first irreversible 8 per cent.

Lowry and Hulett ³ differ from other observers in obtaining a definite break in the sorption curves for water with a number of gas-mask charcoals, which they interpret as marking the filling of the capillaries with liquid water, the remaining increase being due mainly to the flattening of the menisci at the ends of the capillaries. From this, neglecting adsorption, they deduce the standard values for the dimensions of the capillaries and their superficial area. It is evident that further experimental work is required to harmonize these deductions with the treatment of the sorption of other vapours, and

¹ A. J. Allmand, P. G. T. Hand, and J. E. Manning, *J. Phys. Chem.*, 1929, **33**, 1710.

² W. Bachmann, *Z. anorg. allgem. Chem.*, 1917, **100**, 1.

³ H. H. Lowry and G. A. Hulett, *J. Am. Chem. Soc.*, 1920, **42**, 1406. H. H. Lowry (*J. Am. Chem. Soc.*, 1924, **46**, 837) found no sharp break for 23 samples of charcoal prepared from anthracite coal.

that their interpretation is directly negated by the expansion experiments of Porter (this chapter, page 148).

Others who have studied the sorption of water vapour by charcoal include Schmidt and Hinteler,¹ Hällström,² Herbst,³ Tryhorn and Wyatt,⁴ Pearce and Knudson,⁵ Lavine and Gauger,⁶ and Selvig and Kaplan.⁷ Wilson and Fuwa's⁸ data for charcoal, carbon black, lampblack and coke are included with those for forty-four other substances in Chapter XII, pages 388 and 389.

SORPTION OF MERCURY VAPOUR BY CHARCOAL

Only recently has the sorption of mercury vapour been studied, although it is important to know whether charcoal does sorb mercury vapour or not since it is frequently present during evacuation and even in the sorption apparatus. It has been taken for granted that since the vapour pressure of mercury is only 0.001 mm., it might be neglected, although this partial pressure in the volume of air inhaled by a man in a day would amount to no less than 0.1 gm. of mercury.

Zelinsky and Rakusin⁹ found that at room temperature birch charcoal exposed to air saturated with mercury vapour took up 5.65 per cent of its weight of mercury, and after prolonged exposure to air free from mercury, still retained 4.69 per cent which distilled off on heating. This experiment shares the ambiguity of all experiments with saturated

¹ G. C. Schmidt and B. Hinteler, *Z. physik. Chem.*, 1916, **91**, 103.

² M. af Hällström, *Dissert.*, Helsingfors, 1920.

³ H. Herbst, *Biochem. Z.*, 1921, **118**, 103.

⁴ F. G. Tryhorn and W. F. Wyatt, *Trans. Farad. Soc.*, 1926, **22**, 134.

⁵ J. N. Pearce and C. M. Knudson, *Proc. Iowa Acad. Sci.*, 1927, **34**, 197; C. M. Knudson, *Dissert.*, State University of Iowa, 1924.

⁶ I. Lavine and A. W. Gauger, *Ind. Eng. Chem.*, 1930, **22**, 1226; M. Larian, I. Lavine, C. A. Mann, and A. W. Gauger, *Ind. Eng. Chem.*, 1930, **22**, 1231.

⁷ W. A. Selvig and B. B. Kaplan, *J. Ind. Eng. Chem.*, 1920, **12**, 783.

⁸ R. E. Wilson and T. Fuwa, *J. Ind. Eng. Chem.*, 1922, **14**, 913.

⁹ N. D. Zelinsky and M. A. Rakusin, *Ber.*, 1926, **59B**, 2072.

vapours in that an indefinite excess may be condensed in bulk.

Coolidge¹ carried out a more systematic investigation, the results of which are summarized in fig. 56 and table 30, which show the isosteres for various numbers of milligrams sorbed by 1 gm. of activated coconut charcoal and the maximum sorption at various temperatures, respectively. At the higher

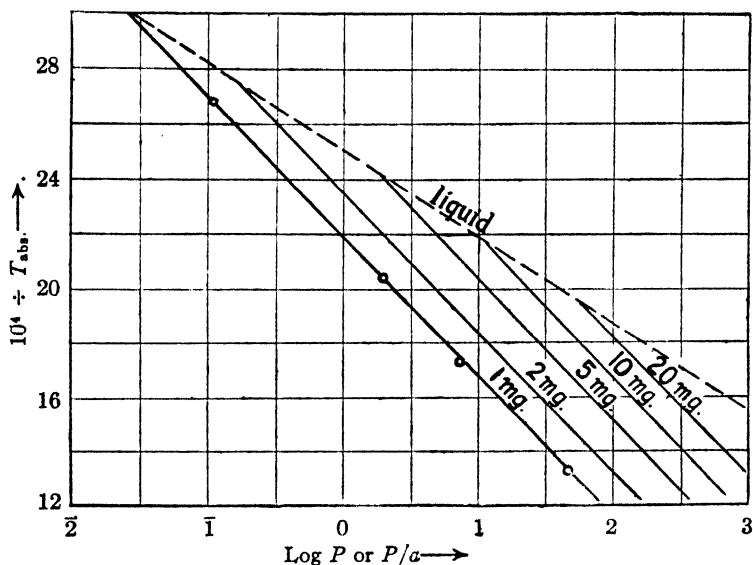


Fig. 56.—Coolidge's Isosteres for Given Weights of Mercury (in mg.) sorbed by Charcoal at various Temperatures and Pressures P (in mm. Hg). The Dashed Curve is the Vapour Pressure of Liquid Mercury.

temperatures, where it could be tested, Henry's law held. The slope of the isosteres, which are parallel, indicate a molar heat of sorption of 8,900 calories which is much less than the heat of evaporation of liquid mercury, 13,000 calories. Hence the transfer from the liquid to the charcoal is strongly endothermic. Therefore it is only at high temperatures, where the vapour pressure is high, that the sorption of mercury

¹ A. S. Coolidge, *J. Am. Chem. Soc.*, 1927, **49**, 1949.

becomes great, rising to 6.9 per cent by weight of the charcoal at the boiling point of mercury. Coolidge demonstrated that at these higher temperatures, the mercury is quite capable of displacing other substances from charcoal.

TABLE 30

Maximum Weights of Mercury Vapour which can be Sorbed by Activated Coconut Charcoal at various Temperatures

° C.	Vapour pressure of liquid Hg	Maximum x/m	° C.	Vapour pressure of liquid Hg	Maximum x/m
20	0.0013	0.3	220	33.7	16
60	0.03	1.2	260	98	24
100	0.28	2.5	300	246	34
140	1.85	5.3	360	790	69
180	9.2	10			

Shiels ¹ found that an extracted German gas-mask charcoal gave results of the order of 0.2 mg. per gram of charcoal like those of Coolidge and only about 1/250 of that obtained by Zelinsky and Rakusin, and he did not detect with certainty any sorption of mercury in the presence of air.

SORPTION OF NOBLE GASES

The sorption of noble gases and radioactive emanations is approximately that to be expected of gases and vapours in general, but it is convenient to collect the chief results obtained for these chemically inactive substances whose sorption is of purely physical type.²

Data have already been cited for the work of Dewar,³ Homfray,⁴ and McLean⁵ with helium. The great difference in the amounts of the ordinary gases of the atmosphere and of neon and helium sorbed by charcoal, owing to the low boiling points of these noble gases, has long been utilized for the demonstration of their presence in air and the extent to

¹ D. O. Shiels, *J. Phys. Chem.*, 1929, **33**, 1398.

² For a brief review of the literature with numerous references, including many not here cited, see K. Peters and K. Weil, *Z. physik. Chem.*, Abt. A, 1930, **148**, 1, 2.

³ Chapter I, page 10; Chapter III, pages 42 and 43.

⁴ Chapter III, page 43; Chapter IV, page 99, fig. 27, and page 100, table 21,

⁵ Chapter III, page 43.

which they occur.¹ Dewar² used it to measure the traces of helium dissolved in various naturally occurring waters, such as rain and sea water. Antropoff³ has devised a simple and striking lecture experiment to show the way in which atmospheric gases are sorbed. Miss Homfray's data show that argon, on the other hand, is sorbed to almost the same extent as nitrogen. Much more extensive data for argon have been obtained by Ruff and Roesner,⁴ a few of whose results were quoted on page 73 of this chapter.

Claude,⁵ using Dewar's method, measured the sorption of nitrogen at -182.5° and of helium, neon and hydrogen at -195.5° . He found that hydrogen was much more sorbed than neon in spite of the opposite order of their condensabilities. His results are not reproduced here because the sorption for hydrogen is so much greater in comparison with helium than in the corresponding experiments of Dewar.

The sorption of argon, krypton and xenon by active charcoal has been studied by Peters and Weil⁶ who used desorption for their quantitative separation. Their isotherms are reproduced in fig. 57,⁷ and values for the constants of the classical equation, $x/m = kp^{1/n}$, are given in table 31. In both cases x/m is expressed in cubic centimetres (at N.T.P.) for 1 gm. of zinc chloride impregnated activated charcoal. As they point out, the regularity of sorption is so great that the determination of one or two points on a single isotherm for, say, argon with a given specimen of charcoal enables a moderately

¹ For example, W. Ramsay, *Proc. Roy. Soc. (London)*, A, 1905, **76**, 111; S. Valentiner and R. Schmidt, *Sitzber. preuss. Akad. Wiss.*, 1905, page 816; *Ann. der Physik* (4), 1905, **18**, 187; J. Satterly *Phil. Mag.*, (6), 1908, **16**, 584.

² J. Dewar, *Compt. rend.*, 1904, **139**, 421; *Chem. News*, 1904, **90**, 73; *Proc. Roy. Soc. (London)*, 1904, **74**, 122.

³ A. von Antropoff, *Ber.*, 1923, **56B**, 2135.

⁴ O. Ruff and G. Roesner, *Ber.*, 1927, **60**, 414.

⁵ G. Claude, *Compt. rend.*, 1914, **158**, 861.

⁶ K. Peters and K. Weil, *Z. physik. Chem.*, Abt. A, 1930, **148**, 1. See also Chapter VI, page 193, footnote 4.

⁷ K. Peters and K. Weil, *Z. physik. Chem.*, Abt. A, 1930, **148**, 19, fig. 4.

accurate prediction to be made of the sorption of each of the noble gases at this low range of temperatures and pressures. Compare, for example, the parallel isobars and isotherms of Miss Homfray for argon, this chapter, page 99.

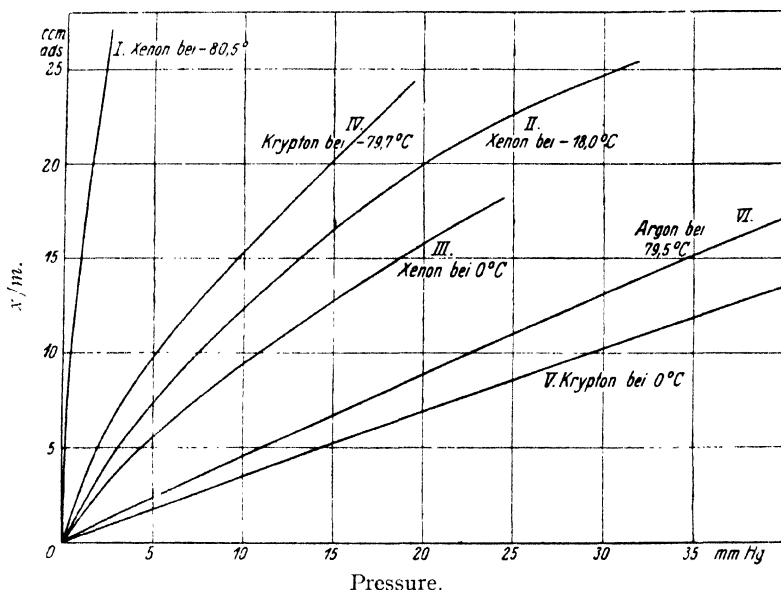


Fig. 57.—Sorption Isotherms for Xenon, Krypton and Argon at Low Temperatures with ZnCl_2 -active Charcoal.

TABLE 31

Constants of the Classical Isotherm for the Sorption of Noble Gases by ZnCl_2 -active Charcoal

Gas	$T = 193^\circ \text{ abs.}$		$T = 255.2^\circ \text{ abs.}$		$T = 273.2^\circ \text{ abs.}$	
	k	$1/n$	k	$1/n$	k	$1/n$
Argon	0.500	0.950	(0.0764)	(1.0)	(0.0581)	(1.0)
Krypton	2.927	0.711	(0.497)	(0.885)	0.340	1.0
Xenon	15.99	0.574	2.458	0.692	1.583	0.77

Isotherms for argon in the neighbourhood of 85° absolute have been obtained for a variety of substances by Hüttig and Juza.¹ Charcoal yielded isotherms of the usual type,

¹ G. F. Hüttig and R. Juza, *Z. anorg. allgem. Chem.*, 1929, **177**, 317.

most of the sorption taking place at low pressure, but those with silica resembled the diagrams of Zsigmondy and van Bemmelen with water, even indicating the same size of pores in the region of hysteresis. Hydrous antimony oxide and different specimens of stannic oxide gave results of intermediate type, whereas active calcium, nickel sulphide and powdered cassiterite did not sorb argon.

The sorption of radium, thorium and actinium emanations was first noticed by Rutherford¹ and has been studied by Boyle² and Mohr.³ Boyle studied radium and thorium emanations at temperatures from 185° C. to -75.5° C. and showed that thorium emanation is appreciably sorbed even at higher temperatures. Coconut charcoal was most efficient, animal charcoal less so, and wood charcoal least.

Mohr's careful study of radium emanation, using coconut charcoal, made use of both a static and a dynamic method extended over temperatures from 500° C., at which sorption was still measurable (7.14 per cent of the emanation present in the current of air), down to -180° C. (100 per cent).

SORPTION OF MIXTURES

Much of the work on sorption has involuntarily concerned itself with the behaviour of mixtures in the form of impurities, and all dynamic measurements are carried out in a current of air or other gas.⁴ We have found that these foreign substances interfere with the sorption of the specified vapour or gas, not so much at high pressures of the latter but very seriously at low pressures. The competition between the

¹ E. Rutherford, *Nature*, 1906, **74**, 634.

² R. W. Boyle, *J. Phys. Chem.*, 1908, **12**, 484; *Phil. Mag.* (6), 1909, **17**, 374. See also C. Porlezza and G. Norzi (*Atti accad. Lincei*, (5), 1911, **20**, 932) who found that the occluded gas of Fiuggi tufa (about 25 c.c. per 200 g. of rock) consists chiefly of carbon dioxide and oxygen with only minute amounts of helium.

³ W. Mohr, *Ann. der Physik* (4), 1916, **51**, 549. A reference to sorption of radium emanation not seen by the writer is H. E. Roth, *Dissert.*, Frankfurt, 1919.

⁴ E. Berl and K. Address (*Z. angew. Chem.*, 1921, **34**, 379) determined in connexion with their experiments the amount of air displaced from charcoal by organic vapours.

various substances is also manifested in the very great increase of time required for the attainment of equilibrium,¹ as indeed, is only to be expected from the consideration that the displacement of the one already in possession frequently has to take place in pores of molecular dimensions.

The questions which most naturally arise concern, first, the selectivity exhibited between the sorption of the constituents of the mixture and, secondly, the comparison between the total sorption and that of the constituents if taken separately.

An excellent example of selective sorption by charcoal which is of essential importance in many applications, as in gas warfare, is the retention of organic vapours with the rejection or replacement of water. Charcoal may sometimes be used even when dripping wet.² This is true selectivity as distinguished from that exhibited in the dynamic measurements under conditions where one of the constituents is very little sorbed anyway. Such measurements, as a first approximation, approach, although they do not quite attain, the same equilibria as in a static measurement.

Much of the earlier work dealt with studies of air, especially at room temperature and atmospheric pressure. For example, Smith in 1863³ obtained the following data in a Fontana experiment, which he summarized in the exaggerated expres-

¹ For an early demonstration that the position of equilibrium may be independent of the order of mixing see Joulin, Chapter I, page 7. (Confirmed by H. B. Lemon and K. Blodgett (*Phys. Rev.* (2), 1919, **14**, 394; *Proc. Nat. Acad. Sci.*, 1919, **5**, 289) but questioned by L. B. Richardson and J. C. Woodhouse (*J. Am. Chem. Soc.*, 1923, **45**, 2638) because they could not attain it in 39 hours.) Joulin also showed that the first apparent effect of an admixture may be an evolution of gas, followed by a slow approach toward equilibrium. This was likewise observed by R. A. Smith (*Proc. Roy. Soc. (London)*, A, 1926, **112**, 296).

² On the other hand, charcoal may, of course, be used for the drying of large quantities of air. See, for example, H. Isobe, *Eng. Chem. J. (Japan)*, 1921, **1**, 99.

³ R. A. Smith, *Proc. Roy. Soc. (London)*, A, 1926, **112**, 297. F. Bergter (*Ann. der Physik*, (4), 1912, **37**, 506) found that at very low pressures and room temperature oxygen is sorbed 30 to 40 times as

sion "charcoal adsorbed oxygen rapidly, leaving nitrogen untouched". He was, of course, working at a temperature sufficiently high for the sorption of oxygen to be irreversible (compare Chapters I, page 9, and IV, pages 69, 120 and 121).

TABLE 32

Selective Sorption by Charcoal from a Mixture of Oxygen and Nitrogen

Original volume		Final volume		Volume sorbed	
Oxygen	Nitrogen	Oxygen	Nitrogen	Oxygen	Nitrogen
12.12	48.18	0.06	37.93	12.12	0.06
16.74	63.76	0.74	63.76	16.00	0.00
32.92	91.08	3.75	68.45	19.35	22.68
16.76	63.91	0.00	42.36	16.76	21.55

Dewar ¹ found that charcoal which had been exposed to a current of air for a long time at -185°C . had sorbed three volumes of oxygen to two of nitrogen. The same result was attained when the charcoal originally contained hydrogen, for this was displaced. However, a current of hydrogen replaced one of the molecules of oxygen by one of hydrogen. Theoretically, of course, a current of any one pure gas should ultimately displace any other from charcoal, the effect being similar to that of evacuation. When Dewar cooled 50 g. of charcoal, it sorbed about 6 litres of air in ten minutes. Upon gradual warming the first litre evolved contained 18.5 per cent oxygen, the second 30.6 per cent, the third 53 per cent, the fourth 72 per cent, and the fifth 80 per cent. Similarly, Lorenz and Wiedbrauck ² found that upon warming much as nitrogen by coconut charcoal. He concluded from his experiments that the presence of oxygen in these small quantities distinctly enhanced the amount of nitrogen sorbed.

¹ J. Dewar, *Proc. Roy. Inst. Gr. Britain*, 1906, **18**, 440; *Chem. News*, 1908, **97**, 4, 16.

² R. Lorenz and E. Wiedbrauck, *Z. anorg. allgem. Chem.*, 1924, **139**, 324. Also further experiments on mixtures, carbon monoxide, carbon dioxide, oxygen, nitrogen and ethylene. In an earlier paper (*Z. anorg. allgem. Chem.*, 1924, **135**, 42) they passed an analysed mixture of oxygen, nitrogen, hydrogen and carbon dioxide over charcoal for various periods, showing that the proportions sorbed varied greatly with the time, hydrogen predominating at first, then carbon dioxide. E. Berl and O. Schmidt (*Z. angew. Chem.*, 1923, **36**, 247) found that three passages over charcoal removed ethylene almost quantitatively from a mixture with methane and nitrogen.

charcoal that had sorbed hydrogen and carbon dioxide, the hydrogen was the first to be given off.

Dewar's measurements bear out two suggestions :

1. That each substance interferes with the sorption of others.¹ One would expect this effect to be least where sorption was least extensive or where there was a large supply of sorbing material. Thus, at 0° C. where oxygen and carbon monoxide were sorbed ² to the extent of 18 and 21 c.c., respectively, when separate, as much as 30 c.c. of the mixture was sorbed. On the other hand, at - 185° C. where the respective quantities separately were 230 and 190 c.c., the total amount of mixture which could be sorbed was only 195 c.c. Evidently, at - 185° C. the charcoal is nearly full in all three cases.

2. In the mixture the substance most readily sorbed is the least affected by the presence of others so that its proportion in the amount sorbed is correspondingly enhanced. Thus in Dewar's case at - 185° C., 230 c.c. of oxygen are sorbed to 155 c.c. of nitrogen when taken separately, each at one atmosphere pressure. This, as we have seen, is the proportion in which they are sorbed from air in which the oxygen has only one-fourth the pressure of the nitrogen.

Miss Homfray ³ found at - 78° C. that the volumes of mixtures of nitrogen and carbon monoxide sorbed by charcoal were intermediate between those for nitrogen and carbon monoxide separately. A similar result was apparent for mixtures of oxygen and hydrogen at the same temperature. Hempel and Vater ⁴ studied mixtures of hydrogen with ethane, methane, ethylene, and acetylene and also nitrogen with

¹ This is confirmed by H. B. Lemon and K. Blodgett (*Phys. Rev.*, (2), 1919, **14**, 394; *Proc. Nat. Acad. Sciences*, 1919, **5**, 289), using small amounts of oxygen and nitrogen at the temperature of liquid air. It was also found to be the case by A. M. Bakr and J. E. King (*J. Chem. Soc.*, 1921, **119**, 454) in the sorption of benzene and iodine by charcoal. J. Driver and J. B. Firth, *J. Chem. Soc.*, 1921, **119**, 1126; alcohol and water by charcoal.

² J. Dewar, *Proc. Roy. Inst. Gr. Britain*, 1905, **18**, 182; *Compt. rend.*, 1904, **139**, 261.

³ I. F. Homfray, *Z. physik. Chem.*, 1910, **74**, 136.

⁴ W. Hempel and G. Vater, *Z. Elektrochem.*, 1912, **18**, 726.

ethylene, using animal charcoal. Hene¹ found that the total volume sorbed at one atmosphere pressure from mixtures of nitrogen and oxygen, nitrous oxide and carbon dioxide, hydrogen and sulphur dioxide, chloroform and sulphur dioxide, hydrogen and nitrogen at room temperature was slightly less than the mean of the volumes of the two gases separately at one atmosphere pressure.

Richardson and Woodhouse² are almost the only investigators who have analysed the gases in the mixtures, before and after sorption, and who have measured and analysed the gases sorbed. They have carried out very careful measurements with nitrous oxide and carbon dioxide alone and together, using steam activated charcoal at 0° C. Their results are remarkable, not only in themselves but in that an important part of their significance seems to have escaped their own attention. Nitrous oxide by itself is rather more sorbed than carbon dioxide under similar conditions except at about 2,850 mm. Hg where they become equal. This disparity in sorption is greatly increased in all the mixtures. For example, in a 50/50 mixture at 2,870.5 mm. Hg there are only 57.3 c.c. of carbon dioxide sorbed to 60.2 c.c. of nitrous oxide, a slight but real discrepancy. As the pressure is lowered the disproportion becomes greater and greater until at about 100 mm. Hg twice as much nitrous oxide as carbon dioxide is adsorbed from the 50/50 mixture.

However, they find that "the formula $V_{mixture} = \frac{V_{N_2O}a_1 + V_{CO_2}a_2}{100}$

in which V_{N_2O} and V_{CO_2} represent the volumes of those gases separately adsorbed at the total pressure of the mixture, and a_1 and a_2 stand for the percentages of the respective gases in the mixture, holds within reasonable limits as shown in Table V" (table 33, page 164).

Since the total volume is thus additive as shown in the table and yet there is a relative deficiency in the amount of carbon dioxide sorbed, especially at the lower pressures,

¹ W. Hene, *Dissert.*, Hamburg, 1927, p. 37.

² L. B. Richardson and J. C. Woodhouse, *J. Am. Chem. Soc.*, 1923, **45**, 2647.

TABLE 33

Volume of Mixture of Nitrous Oxide and Carbon Dioxide adsorbed, calculated from Separate Adsorption Curves, compared with Values experimentally obtained

Pressure mm.	" 50-50 mixt."		" 75-25 mixt."		" 25-75 mixt."	
	Calc.	Obt.	Calc.	Obt.	Calc.	Obt.
2,800	118.3	117.1	118.4	118.4	118.3	118.5
1,600	104.2	102.4	102.2	102.3	106.4	105.8
1,000	89.7	88.7	87.3	87.0	92.3	91.9
600	73.4	73.2	70.6	70.2	76.5	75.1
200	44.1	43.7	41.7	41.4	46.7	47.1

there must be an equally great enhancement of the sorption of nitrous oxide through the presence of carbon dioxide at low pressures. This is in conflict with Rule 1 above, but it is in agreement with the result of Bergter¹ for nitrogen and oxygen at low pressures to which other authors have not given credence. See also the suggestion made by Shah (Chapter IV, page 125) that nitrous oxide is sorbed by sorbed oxygen; and also by Allmand and Chaplin² that sufficiently high pressures will cause sorption of carbon tetrachloride upon charcoal covered with oxygen in much the same manner as on cleaned up charcoal surfaces, but that such sorbed vapour will come off regularly on reducing the pressure whereas that sorbed by clean charcoal will not.

Freundlich³ has indicated that Tryhorn and Wyatt⁴ observed a similar result; however, the experimental basis for the comparison with sorption of the separate substances at the same pressure appears to be entirely lacking, since Tryhorn and Wyatt dealt only with saturated vapours. They used unevacuated coconut charcoal at 20°, exposed in presence of air to the saturated vapour of mixtures of benzene with alcohol or with acetone. In all cases the proportion of alcohol was greater in the charcoal than in the vapour phase, but

¹ Page 160, footnote 3.

² A. J. Allmand and R. Chaplin, *Proc. Roy. Soc. (London)*, A, 1930, **129**, 264.

³ H. Freundlich, *Kapillarchemie*, 1930, Bd. I, p. 195, footnote 7.

⁴ F. G. Tryhorn and W. F. Wyatt, *Trans. Farad. Soc.*, 1925, **21**, 399.

this was true of acetone only up to 72 mols per cent, after which the relation was reversed. Comparison with the composition of the liquid instead of the vapour phase¹ shows that the same data may be interpreted as negative sorption of the alcohol and acetone above 20.5 and 33.3 mols per cent respectively.

Tryhorn and Wyatt interpret these and further² similar experiments with binary mixtures in terms of the classical de Saussure-Polányi theory (Chapter XVII). They find that for the first few hours the vapour is taken up as a whole. Thereupon follows an adjustment in the composition of the sorbed vapour, sometimes without much increase in the amount of sorption. This is followed by slow prolonged increase in sorption, the composition likewise slowly altering. They attribute the second stage to a condensation of the sorbed vapours to the form of sorbed liquid and the final stages and further condensation to bulk liquid in the intergranular spaces (Chapter XVI). However, they leave out of account the air space and the effect of the air therein, although this undoubtedly plays a dominant rôle in the diffusion processes. For example, Bakr and King in the writer's laboratory observed that when a sealed-up tube about 20 cm. long terminates with a bulb at each end and one of the bulbs contains a few cubic centimetres of benzene at 100° C. and the other is kept at 25° C., it required about a week for the benzene to distil into the cooler bulb through the cushion of air.

Magnus and Roth³ observed another anomaly in that when they passed mixtures of carbon dioxide and hydrogen (with some air) over charcoal at temperatures between 0° and 150°, they observed at first an increase in the sorption of hydrogen with increase in partial pressure in the gas, but this was followed by a maximum beyond which the sorption of hydrogen diminished as its partial pressure increased. Some special

¹ F. G. Tryhorn and W. F. Wyatt, *Trans. Farad. Soc.*, 1926, **22**, 143.

² F. G. Tryhorn and W. F. Wyatt, *Trans. Farad. Soc.*, 1928, **24**, 36. (Benzene with methyl, ethyl, propyl and normal butyl alcohol.)

³ A. Magnus and H. Roth, *Z. anorg. allgem. Chem.*, 1926, **150**, 321.

mechanism will be necessary in order to reconcile this with the requirements of thermodynamics.

Lorenz and Wiedbrauck ¹ have studied carbon dioxide alone and in admixture with hydrogen, carbon monoxide and ethylene. The sorption of the carbon dioxide is depressed in this order, hydrogen having the least effect. The isotherms for ethylene and carbon dioxide in the mixture are of different form so that at low pressures the sorption of ethylene is greater than that of carbon dioxide whilst at higher pressures this relation is reversed. They attribute this to a specific sorption of the unsaturated hydrocarbon by secondary valencies while at higher pressures the physical influences corresponding to the higher boiling point and critical temperature of the carbon dioxide predominate.

Reichinstein's ² displacement principle has not been compared directly with the data for mixtures. However, its fundamental assumption that the ratio of the amounts of two substances is directly proportional to their ratio in the mixture of gas, does not allow for, or accord with, the selective adsorption which has been shown in the foregoing discussion to be of common occurrence.

¹ R. Lorenz and E. Wiedbrauck, *Z. anorg. allgem. Chem.*, 1925, **143**, 268.

² D. Reichinstein, *Z. Elektrochem.*, 1913, **19**, 672, 914; 1914, **20**, 406; 1915, **21**, 359; *Trans. Farad. Soc.*, 1913, **9**, 239; Monograph, *Die Eigenschaften des Adsorptionsvolumens*, Verlag Gebr. Leemann & Co., Zurich and Leipzig, 1916; *Z. physik. Chem.*, 1920, **95**, 457; 1921, **99**, 275; 1922, **106**, 209; 1923, **107**, 109; *Z. Elektrochem.*, 1925, **31**, 593; *Z. anorg. allgem. Chem.*, 1927, **168**, 189; P. Bernays, *Z. Elektrochem.*, 1927, **33**, 170. Reichinstein's general adsorption equation is $x/m = k(1 - e^{-P/P_0})$ where each of these terms has the same significance as in the classical isotherm (*Z. Elektrochem.*, 1915, **21**, 371).

CHAPTER V

SORPTION BY CHABASITE, OTHER ZEOLITES AND PERMEABLE CRYSTALS

THE NATURE OF ZEOLITES

Studies of sorption by zeolites, although as yet comparatively few, deserve a special chapter because of the profound influence that they are exerting upon current conceptions of sorption.

Zeolites are hydrous calcium aluminium silicates, some of which exhibit two remarkable properties. Crystals of zeolites may be reversibly dehydrated without any change in transparency or in the sharpness of their crystal form.^{1,2} There-

¹ A. Damour, *Ann. mines*, (3), 1840, **17**, 191; *Ann. chim. phys.*, (3), 1845, **14**, 97; (3), 1858, **53**, 438; Malaguti and Durocher, *Ann. mines*, (4), 1846, **9**, 325; E. Mallard, *Bull. soc. minéral. France*, 1882, **5**, 255; W. Klein, *Z. Kryst. Mineral.*, 1884, **9**, 54; G. Friedel, *Bull. soc. franc. minéral.*, 1896, **19**, 14, 94, 363; 1898, **21**, 5; 1899, **22**, 5; F. Rinne, *Neues Jahrb. Mineral. Geol.*, 1887, II, 17; 1897, II, 28; G. Tammann, *Wied. Ann. der Physik*, 1897, **63**, 16; *Z. physik. Chem.*, 1898, **27**, 323; *Nachr. Ges. Wiss. Göttingen*, 1918, p. 190; F. Grandjean, *Compt. rend.*, 1909, **149**, 866; *Bull. soc. franc. minéral.*, 1910, **33**, 5. Tammann showed that the vapour pressure is a continuous function of the composition. For a summary of earlier literature, see C. Doelter, *Physikalisch-chemische Mineralogie*, Leipzig, 1905, p. 168; *Handbuch der Mineralchemie*, 1921, **2**, *Dritter Teil*, p. 1; and for a summary with regard to the structure, W. Eitel, *Physikalisch-chemische Mineralogie und Petrologie*, Dresden and Leipzig, 1925, p. 104. For a summary of the literature on the hydration of zeolites, especially heulandite, with sixty-eight references and a recalculation and graphical comparison of previous work, see K. H. Scheumann, *Ber. Verhandl. sächs. Akad. Wiss.*, Leipzig, Math.-phys. Klasse, 1921, **73**, 3-113; *Mitt. Inst. Mineral. Petrogr.*, Der Universität Leipzig, No. 140.

² J. R. Katz (*Ergebnisse exakten Naturwiss.*, 1924, **3**, 323, 324, 333, 378, 393) gives the following list of crystals that swell and dehydrate

upon they readily sorb gases and certain vapours. On the other hand, like the amorphous permutit and other artificial zeolites, they exhibit the property of base exchange when immersed in salt solutions. Those commonly studied are chabasite ($\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 6\text{H}_2\text{O}$), heulandite ($\text{CaAl}_2\text{Si}_6\text{O}_{16}\cdot 5\text{H}_2\text{O}$), analcite ($\text{NaAlSi}_2\text{O}_6\cdot \text{H}_2\text{O}$), etc.¹

The zeolites are primarily three dimensional networks ² of oxygen and silicon in which a certain proportion of the silicon is replaced by aluminium, giving a silica-like arrangement of linked tetrahedra with a total negative charge which is locally balanced by the incorporation of other metallic atoms. The

reversibly without losing crystal form and with continuous change of vapour pressure : zeolites, strychnine sulphate, basic zirconium oxalate, cerium oxalate, oxalates of other rare earths, quercitrin and other flavonol derivatives and glucosides, carbon monoxide hæmoglobin, hæmoglobin, edestine and vitelline. For isotherms see Katz, loc. cit., pp. 376 and 393. To this list should be added crystalline magnesium platino cyanide (G. Tammann, *Wied. Ann. der Physik*, 1897, **63**, 16). A. Johnsen (*Neues Jahrb. Mineral. Geol.*, 1903, II, 93) and G. Tschermak (*Sitzber. Akad. Wiss. Wien, Math.-naturwiss. Klasse*, 1912, **121**, IIB, 779 ; 1917, **126**, I, 541 ; 1918, **127**, I, 177) give a summary of the literature on crystals with continuous curves of dehydration including $\text{KOH}\cdot 2\text{H}_2\text{O}$. G. F. Hüttig (*Fortschritte Chem., Physik, physik. Chem.*, 1924, **18**, Heft 1) surveys a number of systems whose isobars or isotherms are more or less continuous, as in zeolites ; amongst these may be mentioned water in pandermite and colemanite, ammonia in iodoform and magnesium halides, and hydrogen in lithium. Further, A. P. Palkin, *J. Russ. Phys.-Chem. Soc.*, 1929, **61**, 2133 ; dehydration of ammonium chromium oxalate. See also W. Biltz and B. Fetkenheuer, *Z. anorg. Chem.*, 1914, **89**, 117 ; W. Biltz and G. F. Hüttig, *Z. anorg. allgem. Chem.*, 1921, **119**, 120 ; W. Biltz, *Z. anorg. allgem. Chem.*, 1923, **130**, 93 ; 1924, **133**, 315). Many other crystals possess unoccupied spaces as, for example, ultra-marine, beryl, etc. Some of these exhibit holes through the crystals as much as 6 Å. in diameter. L. Pauling (*Proc. Nat. Acad. Sci.*, 1930, **16**, 453) has shown by means of X-rays that the structure of natrolite (sodium aluminium silicate) is such that water can escape on heating through channels along (001), along which also sodium ions escape in base exchange.

¹ For a general review see M. H. Hey, *Mineralog. Mag.*, 1930, **22**, 422.

² See for example, W. L. Bragg, *Nature*, 1930, **125**, 510.

silicon is found at the centre of a regular tetrahedral group of oxygen atoms which are 1.6 Å. distant from the silicon and 2.6-2.7 Å. from each other.¹ The incorporated metallic ions are attached to the oxygen atoms which have only one linked silicon and are indifferent to oxygen atoms which are linked to two atoms of silicon.²

MOLECULAR SIEVES AND PERSORPTION

Great interest attaches to the finding of Weigel and Steinhoff³ that chabasite rapidly sorbs the vapours of water, methyl and ethyl alcohol, and formic acid, whereas acetone, ether and benzene are largely excluded. The significance of their results was pointed out by McBain⁴ and recognized by all later writers. It is evident that the partially dehydrated chabasite forms a nearly perfect molecular sieve or a semi-permeable membrane of extremely regular structure. The substances which Weigel and Steinhoff found to be rapidly taken up have small molecular volumes, whereas those whose vapours are excluded have molar volumes greater than about seventy-six. McBain therefore deduced that the pores of chabasite are of less than 5 Å. in diameter,⁵ whereas with later information O. Schmidt⁶ estimates their diameter as 3.5 Å., being the effective molecular diameter of ethylene. The porosity therefore rivals that of an ideally activated charcoal

¹ Compare the typical interatomic distances and molecular diameters quoted in Chapter IV, page 82, table 13.

² I. Masson (*Trans. Farad. Soc.*, 1928, **24**, 169) states that "H. B. Baker showed in 1910 that water vapour will not pass through a naturally-anhydrous salt-crystal, but will pass through a crystal of a hydrated salt".

³ O. Weigel and E. Steinhoff, *Z. Krist.*, 1925, **61**, 125.

⁴ J. W. McBain, *Colloid Sym. Mon.*, (Mass. Inst. Tech., 1926), 1926, **4**, 1; *Kolloid-Z.*, 1926, **40**, 1. The interesting results obtained in the Harvard laboratory by A. B. Lamb and his collaborators from 1926 onwards are still unpublished.

⁵ Other zeolites, according to the observations of F. Grandjean, using iodine, air, bromine, mercury, ammonia, calomel, etc., appear to be of finer porosity (*Compt. rend.*, 1909, **149**, 866; *Bull. soc. franc. minéral.*, 1910, **33**, 5).

⁶ O. Schmidt, *Z. physik. Chem.*, 1928, **133**, 280.

and is surpassed perhaps only by that of siloxene.¹ For example, Schmidt points out that the superficial area of the sum total of the water vapour molecules contained in 1 kg. of chabasite amounts to about four million square metres, a figure which may be compared with those adduced in Chapter I.

We have here a model of fully developed persorption, where the interstices or ultrapores or spaces within the crystal lattice, which are not already filled with the material of the crystal itself, may hold indifferently any molecules which are small enough to enter them and permeate the crystal. There is still a real distinction between such a system and that of an ordinary crystal such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ where the water is an integral part of the structure and bears some chemical relationship to the other substances contained in the crystal. On the other hand, persorption more closely resembles a solid solution in that the sorbed material is disseminated throughout all the available space of the crystal, without, however, displacing the atoms which permanently make up the structure of the crystal. This latter fact constitutes the distinction between persorption and true solution where every part of the space within the solution is at some time or other indiscriminately occupied by molecules of solute. The distinction appears more clearly in imperfectly porous bodies such as active charcoal where portions of the charcoal and any unoccupied spaces therein are permanently inaccessible to the sorbed material.

Again, the reason that dehydrated zeolite sorbs vapours, whereas hydrated zeolite does not, quite evidently is dependent upon simple mechanical displacement, the vapour occupying the spaces set free by the removal of the water molecules. This is very distinctly different from the behaviour designated as salting out in real solutions, and the term solid solution is a misnomer.

¹ The insoluble product obtained by interaction of acids with CaSi_2 , which has the formula $\text{H}_6\text{Si}_6\text{O}_8$; see H. Kautsky, *Z. Elektrochem.*, 1926, **32**, 349; H. Kautsky and G. Blinoff, *Z. physik. Chem.*, Abt. A, 1928, **139**, 497 (see also this chapter, page 175).

Having recognized this distinction between solid solution and persorption, even in the case of a zeolite, we see also the artificiality of the conception of "adsorption" upon the so-called interior surface in such a case.¹ A somewhat parallel picture to "persorption" with charcoal is given by Evans and Bannister² in describing the growth of thick silver iodide films upon silver. "Iodine passes through pores of a few molecular diameters in loose union with the silver iodide—a process intermediate in character between diffusion in solid solution and gaseous leakage through definite cracks."

SORPTION OF WATER AND OTHER VAPOURS

Tammann³ observed that the aqueous vapour pressure of zeolites changes continuously and reversibly with their water content. He determined isotherms for eleven zeolites, allowing about five days at room temperature above a solution of sulphuric acid for attainment of equilibrium. The isotherms have the usual form, characteristic for sorption, with a point of inflection in the neighbourhood of saturated vapour.

Friedel⁴ showed that chabasite which is fully dehydrated (having lost 22.28 per cent by weight of water) sorbs air to the extent of 2.7 per cent of its original weight. However, if not more than 7 or 8 per cent of water has been removed from the chabasite, practically no air is sorbed. In the same paper he obtained three isobars for water vapour and chabasite between temperatures of 0° and 600° C. Previously,⁵ he had shown that the heat of sorption of water vapour by analcite

¹ Nearly all who have studied sorption by zeolites agree that "adsorption" is an inadequate description of the action taking place and they prefer to regard it as a form of solid solution or even chemical combination. The point of view so expressed, however, is embraced in the term "persorption" without confusing previous conceptions of solid solution and chemical combination.

² U. R. Evans and L. C. Bannister, *Proc. Roy. Soc. (London)*, A, 1929, **125**, 370.

³ G. Tammann, *Wied. Ann. der Physik*, 1897, **63**, 16; *Z. physik. Chem.*, 1898, **27**, 323.

⁴ G. Friedel, *Bull. soc. franc. minéral.*, 1899, **22**, 5.

⁵ G. Friedel, *Bull. soc. franc. minéral.*, 1898, **21**, 5.

is far greater than the heat of condensation and that its volume diminishes by about one per cent during the loss of 7 per cent of water. Indeed, as has long been known, dehydrated zeolite disintegrates to a powder if suddenly placed in water, owing to the local heating and expansion.

Seeliger and Lapkamp¹ found that repeated heating of evacuated chabasite to 400° C. reduced its sorbing power for gases to a constant value about 70 per cent of that originally found. They studied isotherms at 0° C. for a mixture of neon and helium, for nitrogen, oxygen, methane, nitric oxide, carbon dioxide, acetylene, hydrogen, and ammonia, finding that their sorption at one atmosphere increased in this order, the order of the respective critical temperatures (with the glaring exception of hydrogen, due to some error such as specific reaction with metals present). The amount of sorption was about as great as with unactivated coconut charcoal, hydrogen again being exceptional; but the rate was much slower, requiring about twenty hours for nitrogen, for example. The mixture of noble gases nearly obeyed Henry's law, but the sorption of ammonia was almost completed at about 50 mm. pressure. The classical sorption isotherm could be applied over only a limited range.

Scheumann² found that the removal of all but the last three molecules of water in heulandite, whether by heat or by diminished pressure at room temperature, is completely reversible but that further dehydration tends to be accompanied by hysteresis. Points on an isotherm for the reversible dehydration in presence of air at room temperature required about 200 days for attainment of equilibrium. He showed that Stoklossa's³ finding that the dehydration took place in eleven or twelve more or less definite steps was erroneous.

¹ R. Seeliger and K. Lapkamp, *Physik. Z.*, 1921, **22**, 563; R. Seeliger, *Z. Physik*, 1921, **4**, 189.

² K. H. Scheumann, *Ber. Verhandl. sächs. Akad. Wiss., Leipzig, Math.-phys. Klasse*, 1921, **73**, 3. See also W. Biltz and E. Rahlfs, *Z. anorg. allgem. Chem.*, 1928, **172**, 273 (sorption of ammonia by partly dehydrated heulandite).

³ G. Stoklossa, *Neues Jahrb. Mineral. Geol., Beilage Band*, 1919, **42**, 1; experiments on six kinds of zeolite.

An isotherm for the sorption of water vapour by chabasite has already been given in Chapter IV, page 145, fig. 52, showing that for carefully evacuated chabasite most of the sorption takes place at extremely low relative pressures of water vapour. There are no other accurately determined isotherms so far published.

Schmidt¹ found that one volume of chabasite at 20° and 760 mm. sorbs the following volumes of gases and vapours:

H ₂	Ar	O ₂	N ₂	CO	CH ₄	CO ₂	NH ₃	H ₂ O
3·3	28·1	34·3	52·2	74·5	80·4	282·0	567·0	702·0

Schmidt expressed his results for various gases by means of the formula quoted in Chapter III, page 56. He pointed out that if various inert sorbing materials such as chabasite, chromic oxide, uranium oxide, vanadium oxide and dehydrated gypsum were compared at any definite temperature and pressure, the relative amounts of the various gases were much the same in each case so that the various solids differed by a roughly constant factor.

Schmidt confirmed the finding of Weigel and Steinhoff that larger molecules such as ether, benzene, and hexamethylene are not sorbed by chabasite; amyl alcohol, butylene and butadiene only slightly; whereas propylene and ethane are on the border line and their sorption is usually much below expectation. Ethylene, whose molecular volume is 44, is freely sorbed. For saturated vapours of water and ammonia the volumes taken up when referred to the liquid condition are approximately equal.

Schmidt's observations are mostly confined to one atmosphere pressure but extend to 400° C. Those of Sameshima² are likewise taken at one atmosphere; at 25° C. 1 g. of heulandite sorbed 138 c.c. (at N.T.P.) of ammonia, 0·5 c.c. of carbon dioxide and 0·2 c.c. of ethylene, this quantity of ammonia being about seven molecules to one molecule of chabasite. Chabasite sorbed 117 c.c. of carbon dioxide, 213 c.c. of ammonia, 58 c.c. of ethylene, and only 1·1 c.c. of

¹ O. Schmidt, *Z. physik. Chem.*, 1928, **133**, 265.

² J. Sameshima, *Bull. Chem. Soc. Japan*, 1929, **4**, 96.

hydrogen as compared with Schmidt's result, 1.5 c.c. (*loc. cit.*). Ethylene was much more slowly sorbed than the other gases.

Baba¹ continued this work with chabasite. Sorption of pentane, benzene, ether, chloroform, carbon tetrachloride, acetone and ethyl acetate was negligibly small; that of ethyl alcohol, ethyl, propyl and butyl amines slight; and that of methyl alcohol, methylamine, carbon dioxide and carbon disulphide (some decomposition) large. The sorption velocities of amine and alcohol are very small in comparison with those of carbon dioxide and carbon disulphide. The chabasite, contrary to Seeliger's experience, improved with repeated sorption of carbon dioxide but may not have reached its full capacity, although as much as forty-four hours was allowed at atmospheric pressure and 25° C.

Simon² allowed two hours for equilibrium at the temperature of liquid oxygen for a maximum pressure of 0.2 mm. of mercury, using argon and nitrogen. He states that the isotherm consisted of a series of straight lines with changes of direction of as much as 75 or 80 per cent at quantities corresponding to each mol of gas taken up by each mol of chabasite. It is very unfortunate that there are no published data on isotherms with zeolites obtained after adequate evacuation and exclusion of air and with values checked both by sorption and desorption. Until then the presumption remains in favour of the smooth isotherms obtained by Tammann, Seeliger and Scheumann already described.

Simon³ indeed found that the molecular heat of absorbed hydrogen at the temperature of liquid hydrogen was equal to that of free hydrogen gas instead of being that of the chemical compound such as he had assumed between argon and chabasite, and nitrogen and chabasite. On the other hand, the

¹ T. Baba, *Bull. Chem. Soc. Japan*, 1930, **5**, 190.

² F. Simon (with J. Schweitzer, G. Glatzel and O. Blüh), *Z. physik. Chem.*, 1928, **132**, 457 (no data given).

³ F. Simon (with J. Schweitzer, G. Glatzel, O. Blüh, J. Aharoni, M. Ruhemann and Miss Ritter), *Z. Elektrochem.*, 1928, **34**, 528; J. Aharoni and F. Simon, *Z. physik. Chem., Abt. B*, 1929, **4**, 186.

magnetic susceptibility of chabasite containing oxygen at 77.6° abs. appeared to show slight changes of direction (*Knicke*) at one and possibly two mols of sorbed oxygen per mol of chabasite. A more distinct and less expected one is found in their data for charcoal.

Grandjean ¹ (loc. cit. page 169, footnote 5) concluded from optical investigations of indices of refraction and pliochromism that the sorbed material in zeolites is anisotropic and oriented. He has also made the interesting comment that substances which are immiscible in the free state are effectually mixed when they are both sorbed within a zeolite.

SILOXENE

Kautsky ² and his collaborators have developed a very interesting study of sorption by siloxene and its derivatives. Siloxene itself has the formula $\text{Si}_6\text{O}_3\text{H}_6$, and it consists of sheets of hexagonal rings of silicon atoms to each of which is attached a hydrogen atom. The hexagonal rings are united by means of oxygen bridges acting through primary valencies. Such a sheet is shown in fig. 58.³ The sheets of silicon atoms are held apart by the hydrogen atoms, thus creating an extremely exposed structure. This is particularly the case owing to the fact that any or all of the hydrogen atoms may be substituted by various other substances such as the halogens or hydroxyl or amino groups, and likewise, through sorption, the lamellæ are thrust further apart. The mother substance,

¹ F. Grandjean, *Compt. rend.*, 1909, **149**, 866; *Bull. soc. franc. minéral.*, 1910, **33**, 5.

² H. Kautsky, *Z. anorg. allgem. Chem.*, 1921, **117**, 209; *Z. Elektrochem.*, 1926, **32**, 349; H. Kautsky and G. Herzberg, *Z. anorg. allgem. Chem.*, 1924, **139**, 135; 1925, **147**, 81; H. Kautsky and H. Zocher, *Z. Physik*, 1922, **9**, 267; *Z. Elektrochem.*, 1923, **29**, 308; *Naturwissenschaften*, 1923, **11**, 194; H. Kautsky and O. Neitzke, *Z. Physik*, 1925, **31**, 60; H. Kautsky and H. Thiele, *Z. anorg. allgem. Chem.*, 1925, **144**, 198; 1928, **173**, 115; H. Kautsky and A. Hirsch, *Z. anorg. allgem. Chem.*, 1928, **170**, 1; H. Kautsky and G. Blinoff, *Z. physik. Chem.*, Abt. A, 1928, **139**, 497.

³ H. Kautsky and G. Blinoff, *Z. physik. Chem.*, Abt. A, 1928, **139**, 498, fig. 1.

calcium silicide, has the same structure of silicon hexagons held together by calcium atoms but like crystalline silicon itself with close packed instead of widely spaced lamellæ. In order to hold the lamellæ of siloxene apart and obtain the open structure it is necessary to have capillary active substances, such as propyl alcohol or propionic acid, present during its formation. The crystalline appearance then dis-

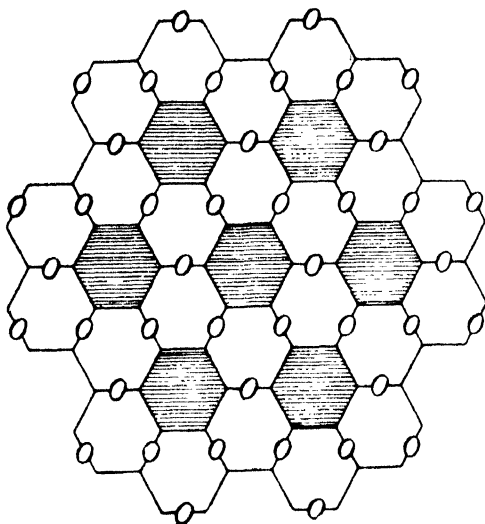


Fig. 58.—The Structure of each Molecular Layer of Siloxene.

appears. However prepared, if the structure is open, the sorption is found to be the same.

Siloxene is not as strongly sorptive as active charcoal or silica gel. A similar material is the silicic acid prepared from biotite or graphitic acid.¹

¹ V. Kohlschütter and P. Haenni, *Z. anorg. allgem. Chem.*, 1919, **105**, 121.

CHAPTER VI

SORPTION BY SILICA, POROUS RIGID JELLIES AND OXIDES

COMPARATIVE BEHAVIOUR OF SILICA AND CHARCOAL

Sorption by silica gel (partially dehydrated jelly of silicic acid) bears the closest relation to sorption by activated charcoal on the one hand and by dehydrated zeolitic crystals on the other. Its mechanism is that designated persorption both for active charcoal and for chabasite. The size of pores is much more under control than is the case with charcoal, and the similarity to chabasite is brought out by the inaccessibility of the interior to larger colloidal particles or molecules.¹

One of the greatest distinctions between sorption by charcoal and by silica gel is that much of the sorption by charcoal takes place at very low relative pressures and is often thereafter increased only to a minor extent with further increase of pressure. With silica and other oxides the amount steadily rises from the lowest pressures; this behaviour is possibly ascribable to the presence of substantial amounts of water in the silica gel, occupying the most active centres, in accordance with the views outlined in Chapter IV in discussing sorption in the presence of impurities. It is for this reason that charcoal excels in the production of high vacua. The steepness of the initial slope of the sorption isotherm has been termed "prehensility" by Briggs; ² he found plum-stone

¹ R. Zsigmondy, *Z. anorg. Chem.*, 1911, **71**, 374 (silica ultrafiltered colloidal silver, benzopurpurine, carmine, and ferric hydroxide but not fuchsine); W. Bachmann, *Z. anorg. allgem. Chem.*, 1917, **100**, 85 (similar ultrafiltration of Prussian blue, before and after addition of sodium chloride).

² H. Briggs, *Proc. Roy. Soc. Edin.*, 1922, **42**, 26.

charcoal best and then, in decreasing order, birch, coconut, and German charcoals, colloidal silica (gel) and activated anthracite. Chaney, Ray and St. John¹ define an equivalent term called "retentivity"; that is, the maximum amount of sorbed vapours which carbon retains or gives off with extreme slowness in a current of air. For various charcoals this is found to be parallel with the sorptive power of iodine from solution.

As was shown in Chapter IV, charcoal readily sorbs organic solvents but not water at low relative pressures. The converse is true of silica.

"That this selectivity of adsorption is a very practical reality is readily demonstrated by the simple experiment of shaking up a mixture of water and benzene, activated carbon and silica gel, respectively. The carbon will adsorb the benzene, and if enough benzene is present to saturate the carbon, the water will be completely rejected. The silica gel will take up the water and reject the benzene."²

Steam displacement is therefore often used in recovering organic solvents from silica gel.³ "It is this selective adsorption of water which destroys the military value of silica gel, ferric oxide gel, and similar hydrophilic adsorbents, and the lack of it that makes carbon of unique and irreplaceable value."⁴ On the other hand, on the principle of "easy come, easy go" the low retentivity of silica for organic vapours is of value in the recovery of solvents.

The retentivity of activated charcoal for carbon tetra-

¹ N. K. Chaney, A. B. Ray and A. St. John, *Ind. Eng. Chem.*, 1923, **15**, 1248.

² N. K. Chaney, A. B. Ray and A. St. John, *Ind. Eng. Chem.*, 1923, **15**, 1250; see also the saturation capacities and break points for benzene, using German and American activated charcoals, silica gel and ferric oxide gel (W. H. Hoffert, *J. Soc. Chem. Ind.*, 1925, **44**, 357T).

³ For practical details see, for example, E. B. Miller, *Chem. Met. Eng.*, 1920, **23**, 1155, 1219, 1251; (ether, acetone, benzene, gasoline, sulphur dioxide, water with silica gel).

⁴ N. K. Chaney, A. B. Ray and A. St. John, *Ind. Eng. Chem.*, 1923, **15**, 1251.

chloride was found to be about 28 per cent by weight, that of silica gel and sil-o-cel 2 per cent or less.¹ Charcoal shows preferential sorption of hydrogen rather than of nitrogen when compared with silica.² On the other hand, silica gel has a specific use in desulphurizing crude petroleum, as also in clarifying oils.

A comparison has been made of the sorptive powers of a number of charcoals and specimens of silica in Chapter IV, page 79, table 12, and also page 85, footnote 1; it will be noted that the specimen of silica prepared by Briggs had double the capacity of the commercial gel. Since the bulk density of silica gel is about 0.8 and that of ferric hydroxide gel is about 1, whereas that of charcoal is nearer to 0.5, much more gel than charcoal can be used in a given container. The bulk density of fifteen silica gels of different origin³ lay between 0.42 and 0.67, those lying between 0.6 and 0.7 having the highest sorbing power by weight as well as by volume. The specific gravity of silica gel in water lies between 2.1 and 2.25.⁴

SILICIC ACID JELLY AND ITS DEHYDRATION

Porous, amorphous minerals are of common occurrence in nature⁵ and include the most varied chemical compounds. Breithaupt (1817) classified amorphous substances as hyaline (glasses) and porodine (guhren or gels). Opal, hydrophane, kieselguhr, chalcedony and agate are among the numerous

¹ N. K. Chaney, A. B. Ray and A. St. John, *Ind. Eng. Chem.*, 1923, **15**, 1250.

² H. Briggs, *Proc. Roy. Soc. (London)*, A, 1921, **100**, 88.

³ E. Bosshard and E. Jaag, *Helv. Chim. Acta*, 1929, **12**, 105.

⁴ J. McGavack and W. A. Patrick, *J. Am. Chem. Soc.*, 1920, **42**, 952.

⁵ A. F. Rogers (*J. Geology*, 1917, **25**, 515) characterizes about twenty, including the halloysite which constitutes the whole or part of some clays, stressing index of refraction. A. Seidenberg's discussion of the difficulty of deciding the true composition of pumice because of the continuity of the desorption and dehydration processes illustrates typical behaviour of such materials (*J. Assoc. Official Agri. Chem.*, 1923, **7**, 98).

forms of silica. It may be suggested that the density, perhaps of the dehydrated mineral, is the best test of porosity.

Many inorganic jellies have been prepared, the essential being to coagulate a hydrous oxide at a suitable rate.¹ Patrick's silica gel is prepared by mixing suitable concentrations of a solution of sodium silicate and hydrochloric acid under violent agitation. After setting to a firm jelly, the material is thoroughly washed and dried in vacuo at temperatures varying between 110° and 300° C., the most active samples being obtained by heating at 250° and nearly 300°.² The silica is thus only partially dehydrated. It is therefore evident that no such careful investigation of the effect of the removal of all impurities can be carried out with silica gel as is possible with the materials described in the two preceding chapters. The experiments are therefore all carried out in the presence of at least water in the gel.

When silicic acid is formed from solution of sodium silicate it occupies the whole volume of the original liquid. Upon dehydration it shrinks very greatly until a clear, dense glass of hardness about 5 remains. Dr. S. S. Kistler³ in collaboration with the author has shown that this is due to the surface tension of the liquid occupying the pores in the loose network of the colloidal particles. It is easy to replace the original water with any other liquid miscible therewith. When the dilute jelly is heated above the critical temperature of the liquid in a closed vessel, every meniscus must disappear. If the former liquid is then allowed to escape slowly as gas, the jelly remains without loss of volume as excessively porous, perfectly transparent material with glossy surface, opalescent by reflected light and exhibiting an extremely low apparent density. This method of retaining jellies in expanded form as aerogels is of general applicability. The effectual operation of surface tension is demonstrated by the fact that when a new liquid such as alcohol flows into this porous material

¹ H. B. Weiser, *The Hydrous Oxides*. McGraw-Hill Book Co., Inc., New York, 1926.

² W. A. Patrick and C. E. Greider, *J. Phys. Chem.*, 1925, **29**, 1031.

³ S. S. Kistler, *Nature*, 1931, **127**, 741.

and is then evaporated, the jelly shrinks to the usual dense, glassy form. A similar increase of porosity but of a lower order of magnitude is obtained by precipitating the silica in the presence of an iron salt whose hydroxide is subsequently removed by acid.¹ Intimate mixtures of carbon with silica gel and metallized silica gels have also been used.² Sorption by the latter is often specific, whereas that by silica gel is non-specific.³

van Bemmelen devoted his classical researches⁴ to the study of the gels and jellies of numerous oxides and hydroxides, including silicic acid. Brewster in 1820, like Maschke in 1872, recognized that the cloudiness or even opacity that prevails during a certain stage of hydration or dehydration is due to porosity, the pores being considered as partly vacuous or filled with air and partly occupied by water.

The usually accepted picture of the structure of a cloudy gel is that due to Zsigmondy and shown in fig. 59⁵ in which the colloidal particles are represented in black, air spaces between them are left white and regions filled with water or organic liquid are washed in in half tone. However, the form and structure of the amicroscopic colloidal particles

¹ H. N. Holmes and J. A. Anderson, *Ind. Eng. Chem.*, 1925, **17**, 280; H. N. Holmes, R. W. Sullivan and N. W. Metcalf, *Ind. Eng. Chem.*, 1926, **18**, 386. E. Berl and H. Burkhardt (*Z. anorg. allgem. Chem.*, 1928, **171**, 120) state that exceptionally active silica gel is obtained from water glass by using aniline hydrochloride.

² For example, N. Shilov, M. Dubinin and S. Toropov (*Kolloid-Z.*, 1929, **49**, 120) who give data for sorption of ammonia, chlorine, water and benzene vapours, comparing them with silica gel and charcoal separately. H. A. Fells and J. B. Firth (*J. Soc. Chem. Ind.*, 1927, **46**, 39T) found maximum sorption for benzene and toluene when the mixed gel ("carbo-gel") contained 18 per cent of carbon.

³ L. H. Reyerson and L. E. Swearingen, *J. Phys. Chem.*, 1927, **31**, 88; isotherms are given for oxygen, carbon monoxide, carbon dioxide, methane and ethylene, hydrogen, hydrogen sulphide, using gels containing silver, platinum, palladium and copper.

⁴ Collected in J. M. van Bemmelen's *Die Absorption*, 548 pages (Theodor Steinkopff, Dresden, 1910); where earlier references are to be found (compare page 192, footnote 1), as also in R. Zsigmondy, *Z. anorg. Chem.*, 1911, **71**, 356.

⁵ R. Zsigmondy, *Z. anorg. Chem.*, 1911, **71**, 360, fig. 1.

themselves are not known. It will be noted that the word "pore" is used in a very special sense by Zsigmondy and others to indicate comparatively large patches of partly filled space. These large patches, which are enormously greater than the colloidal particles or the interstices between the latter, are responsible for the cloudiness or opacity.

Bancroft¹ summarizes the macroscopic observations on silicic acid jellies as follows:

"A dilute jelly may contain about 300 mols of water to one of silica (1 per cent SiO_2). Such a jelly flows together again when broken into pieces. When the water content is only 30-40 mols (10 per cent SiO_2), the jelly can be cut and will stand alone. With 20 mols (14 per cent SiO_2) the jelly is stiff, and it is brittle when the content is 10 mols (1.5 per cent SiO_2). At 6 mols the jelly can be pulverized and the powder is apparently dry. The vapour pressure is practically that of pure water down to a water content of 6 mols per mol of silica. On further dehydration the vapour-pressure curve drops continuously with no sign of the existence of any definite compound. When the water content drops to somewhere usually between 1.5 and 3.0 mols (60 per cent SiO_2) with different samples (point *O* in fig. 60), the jelly becomes opaque and chalky but clears up again when the water content reaches about 0.5-1.0 mol (80 per cent SiO_2) (point *O*₁ in fig. 60). The cloudiness begins when the first air bubbles appear in the pores and lasts until the pores are filled completely with air. Owing to the action of capillarity, the water which evaporates from the outer surface of the capillaries is at once replaced from the inside of the jelly, leaving a vapour space in the centre of the jelly. This produces an opacity which lasts until the pores are free from capillary water. The balance of the water, 0.5-1.0 mol, is probably adsorbed."

van Bemmelen,² summarizes typical observations on the course of dehydration in fig. 60. The observations were made in the presence of air by exposing the specimens of silicic acid in desiccators to about thirty-six different concentrations of sulphuric acid. They were taken out and weighed daily until they appeared constant.

The actual position of the curves on the diagram depends

¹ W. D. Bancroft, *Applied Colloid Chemistry*, p. 330. McGraw-Hill Book Co., Inc., New York, 1926.

² J. M. van Bemmelen, *Die Absorption*, p. 232, fig. 6.

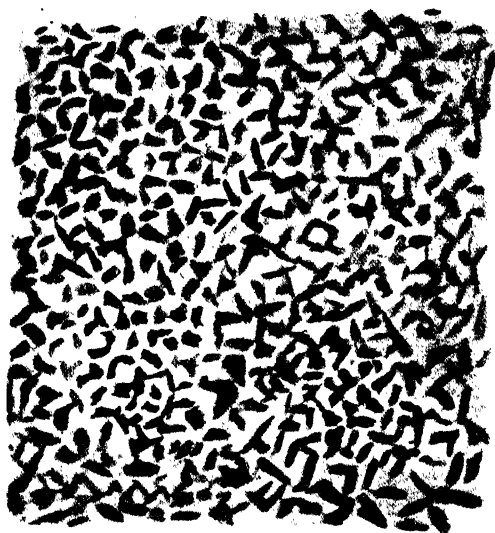


Fig. 59. Structure of a cloudy silica gel.
■—colloidal particles, □—air spaces, □:—water
or organic liquid.

greatly upon the method of preparation, the previous history and the age of the gel or jelly. Starting with a silicic acid jelly whose vapour pressure is indistinguishable from that of water, beyond the right of the diagram, one may follow the dehydration along the dotted path. As is indicated by the single arrow pointing to the left, this path is irreversible and may be followed only once. If the dehydration is interrupted at any point and the attempt made to rehydrate, the vapour pressure rises steeply along the dotted path marked with two

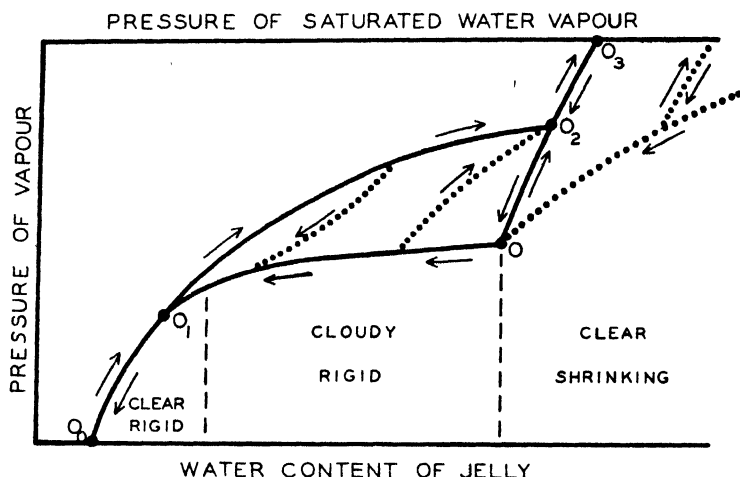


Fig. 60.—The Course of Dehydration of Silicic Acid Jellies (van Bemmelen).

arrows. If dehydration is pursued further, the point O is attained and thereafter hydration and dehydration are accomplished up and down the reversible path OO_2O_3 . Point O is called the *Umschlagspunkt* because at approximately this point the cloudiness appears when further dehydration is attempted. A large amount of water may be removed with relatively little lowering of vapour pressure along the curve OO_1 . If water vapour is again added, the path followed is now O_1O_2 and the jelly is again on the reversible path OO_2O_3 . Beyond O_1 dehydration is again reversible. The region of

hysteresis OO_1O_2 may be crossed in either direction from intermediate points as is indicated by the dotted lines with their accompanying single arrows. Zsigmondy, Bachmann and Stevenson¹ consider that the hysteresis loop OO_1O_2O is due to sorbed air preventing the water from wetting the

capillaries readily or it may more probably be due to entrapped air or vapour.

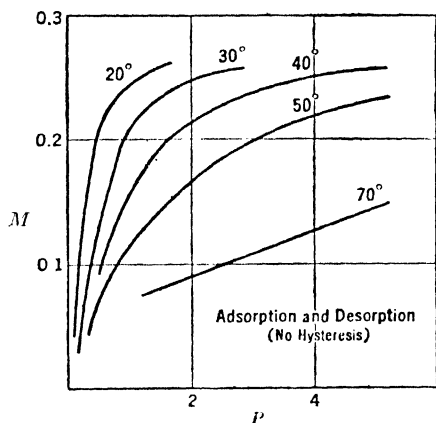


Fig. 61.—Form of Isotherms for Hydration and Dehydration of Silica Gel when Air has been Eliminated (M — grams of water sorbed per gram of gel; P — equilibrium pressure of water vapour).

EFFECT OF PRESENCE OF AIR

No such hysteresis is observed with carefully evacuated silica gel and a smooth reversible isotherm is obtained, but when air is present the hysteresis appears.² Although for the specific case of water this was questioned by Urquhart,³ it is maintained by Patrick, Davis and Barclay⁴

whose isotherms for water, on account of their significance, are reproduced in fig. 61.⁵ The original sample of silica gel

¹ R. Zsigmondy, *Z. anorg. Chem.*, 1911, **71**, 356; *Kolloidchemie*, 5^{te} Aufl., Bd. II, p. 76 (O. Spamer, Leipzig, 1927); R. Zsigmondy, W. Bachmann and E. F. Stevenson, *Z. anorg. Chem.*, 1912, **75**, 189; W. Bachmann and L. Maier, *Z. anorg. allgem. Chem.*, 1928, **168**, 61.

² J. McGavack and W. A. Patrick, *J. Am. Chem. Soc.*, 1920, **42**, 946; W. A. Patrick, *Kolloid-Z., Ergänzungsband*, 1925, Zsigmondy Festschrift, 273; *Colloid Sym. Annual* (Johns Hopkins 1929), 1930, **7**, 129.

³ A. R. Urquhart, *J. Textile Inst.*, 1929, **20**, 117T.

⁴ W. A. Patrick, P. B. Davis and E. H. Barclay, *Colloid Sym. Annual*, (Johns Hopkins, 1929), 1930, **7**, 130.

⁵ W. A. Patrick, P. B. Davis and E. H. Barclay, *Colloid Sym. Annual*, (Johns Hopkins, 1929), 1930, **7**, 131, fig. 2.

had been previously evacuated at 350° "until no further gases were evolved". After introducing portions into the apparatus, they were repeatedly evacuated at 100° C. for from 10–12 hours, meanwhile being exposed each time at room temperature to water free from air. The isotherms were then completely reversible.

Lambert and Clark¹ have rendered a similar service for isotherms of benzene in silica gel (see this chapter, pages 187–189).

It is most interesting to observe that the form of these isotherms for water in the absence of air and volatile impurities differs wholly from those previously obtained and resembles ordinary isotherms for charcoal. This is in accordance with the expectations from the discussion in Chapter IV of the effects of impurity in suppressing sorption, especially in the initial portions of the isotherm. Patrick holds that van Bemmelen and Zsigmondy's collaborators were not dealing with true equilibria. Air here plays almost as decisive a rôle as do the impurities in charcoal. Patrick, however, adds that dynamic methods produce in the case of silica gel a more nearly correct result² than is obtainable in the case of charcoal. His isotherms by the static method after evacuation of the silica gel at 300° C., using sulphur dioxide, ammonia, butane, carbon dioxide, nitric oxide and numerous vapours, resemble those here shown for water, and they exhibit no hysteresis or points of inflection. To the author, it appears probable that if the drastic methods of evacuation discussed in Chapter IV were here available, the sorption isotherms would approach in form those developed for charcoal by means of the sorption balance, practically all the sorption taking place at extremely low pressures. The incompatibility of such behaviour with the hypothesis of sorption as capillary condensation has already been mentioned.

CHEMOSORPTION OR HYDRATES ?

van Bemmelen and most subsequent authors have considered that these curves disprove the existence of definite hydrates

¹ B. Lambert and A. M. Clark, *Proc. Roy. Soc. (London)*, A, 1927, **117**, 183; 1929, **122**, 497.

² W. A. Patrick and L. H. Opdycke, *J. Phys. Chem.*, 1925, **29**, 601.

or hydroxides of silica and the numerous other jelly forming oxides because they represent continuous changes in composition with change in vapour pressure instead of yielding the series of horizontal and vertical lines expected of the phase rule diagram for massive crystalline hydrates of definite composition.¹ However, the writer would point out that this deduction is not valid on account of the porous nature of the products here discussed. Even purely chemical combina-

¹ But compare the attempts, many regarded as successful, to prepare or isolate definite hydrates by such means as using non-aqueous solvents such as acetone and liquid ammonia. The dehydration curve of some of these products was stepwise. See W. Biltz and E. Rahlfs, *Z. Elektrochem.*, 1927, **33**, 491; *Z. anorg. allgem. Chem.*, 1928, **172**, 273; P. Pascal, *Compt. rend.*, 1924, **178**, 481; R. Willstätter and H. Kraut, *Ber.*, 1923, **56B**, 149, 1117; 1924, **57B**, 58, 1082; R. Willstätter, H. Kraut and W. Fremery, *Ber.*, 1924, **57B**, 63, 1491; R. Willstätter, H. Kraut and O. Erbacher, *Ber.*, 1925, **58B**, 2448, 2458; R. Willstätter, H. Kraut and K. Lobinger, *Ber.*, 1925, **58B**, 2462. G. Tschermak (*Sitz. Akad. Wiss. Wien, Math.-Naturwis.-Kl.*, 1912, **121**, 11b, 785; *Monatsh.*, 1912, **33**, 1087) from changes in rate of desorption assumed the existence of a number of definite hydrates. B. L. Vanzetti (*Atti ist. Veneto*, 1915-16, **75**, 261; 1916-17, **76**, 287; *Gazz. chim. ital.*, 1917, **47**, I, 167) employed freezing but adhered to van Bemmelen's interpretation. H. W. Foote and B. Saxton (*J. Am. Chem. Soc.*, 1916, **38**, 588; 1917, **39**, 627, 1103) review the literature on the freezing method as applied to inorganic hydrogels, such as alumina, silica, ferric oxide and lampblack, and greatly extend it, using a dilatometer; concluding that some of the water is combined; for criticism and further references see also E. A. Fisher, *J. Phys. Chem.*, 1924, **28**, 360. Careful studies have been made by A. Simon and his collaborators on the constitution and properties of hydrogels, including isobaric curves of dehydration and X-ray examination. The final stable condition upon ageing is the anhydrous dioxide for silicon, thorium, tin, zirconium, manganese and lead, whereas with alumina, chromic oxide and the pentoxides of antimony and arsenic stable hydrates are formed (*Kolloid-Z.*, 1925, **36**, Zsigmondy Festschrift, 65; 1928, **46**, 161; *Z. anorg. allgem. Chem.*, 1925, **149**, 101; 1927, **161**, 113, 143; 1929, **185**, 101, 107, 130, 280). H. Gaunt and F. L. Usher (*Trans. Farad. Soc.*, 1928, **24**, 32), using strong acids as reference substances, deduced from the concentration of the synergetic liquid from silica jelly that one mol of water is combined with one mol of silica; J. Ferguson and M. P. Applebey (*Trans. Farad. Soc.*, 1930, **26**, 642) show that the hydration is nearly doubled when the *pH* equals 10.

tion, if it is occurring on an exposed surface or, as here, in pores of molecular fineness, obeys the laws of sorption and not those of heterogeneous chemical equilibrium (see Chapter XVIII). Even the fact that the point O_1 in fig. 60 may occur at less than one mol of water to one mol of silica does not invalidate this conclusion, because the curve of sorption (chemisorption) cannot be quite complete until the vapour is saturated. In other words, the chemisorption must be progressive to the top of the diagram even if it is largely completed in the lower part of the diagram. Not until O or O_2 , respectively, do all pores contain liquid, and that under tension. Zsigmondy was in error in assuming that adsorption took place only along O_1O_0 .

JELLIES WITH OTHER LIQUIDS

Graham substituted alcohol, sulphuric acid, nitric acid, and formic acid for water in a silicic acid jelly. van Bemmelen replaced the water by acetone, and Bachmann by benzene, chloroform, ethyl iodide and acetylene tetrabromide. These replace each other at point O in equal volumes. For example, one gel studied by Bachmann¹ took up 2.08, 0.427, and 0.320 mols of water, benzene and acetylene tetrabromide, respectively, per mol of silica corresponding to the volumes 228 c.c., 230 c.c., and 226 c.c. of pore space, respectively. The hysteresis loops found by Anderson² for a given gel with water, alcohol and benzene, respectively, are shown in fig. 62; it will be noted that points O and O_2 , at which the pore volumes are assumed to be full of liquid, come at about the same volume for all three liquids. Using the formula quoted in Chapter XVI, page 433, the pore radius calculated at point O for water, alcohol and benzene came to 26, 25 and 28 Å., respectively, and at O_1 14, 12 and 14 Å. It will be noted that fig. 62 includes the completely non-polar liquid benzene.

Lambert and Clark³ have carried out very careful deter-

¹ W. Bachmann, *Z. anorg. Chem.*, 1912, **79**, 202.

² J. S. Anderson, *Z. physik. Chem.*, 1914, **88**, 212.

³ B. Lambert and A. M. Clark, *Proc. Roy. Soc. (London)*, A, 1927, **117**, 183; 1929, **122**, 511.

minations with benzene. They laid particular stress upon evacuation but unfortunately omitted the precaution of

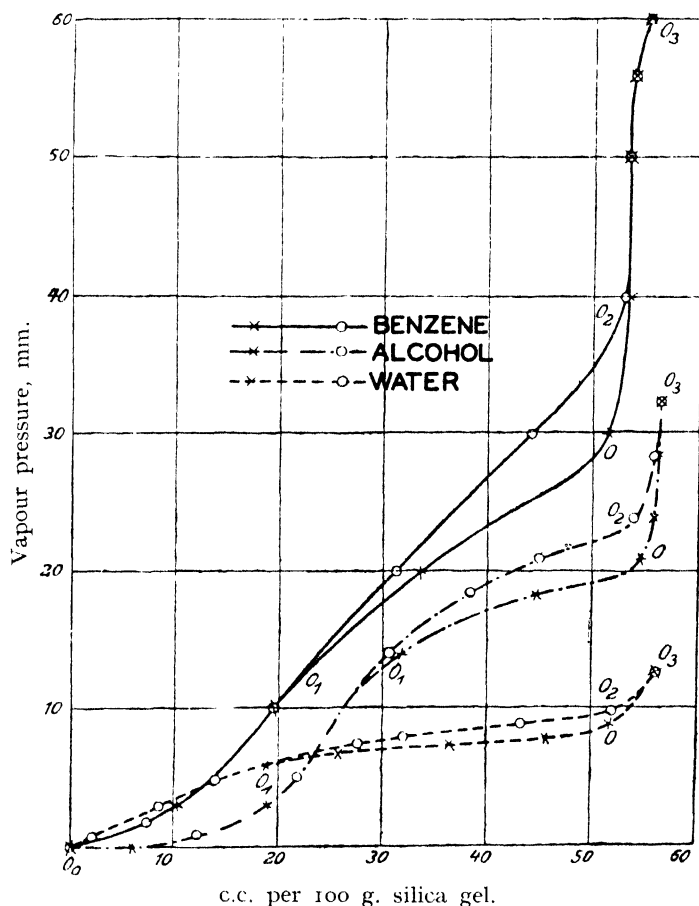


Fig. 62.—Sorption by Silica Gel, showing Hysteresis Loops (Anderson).

washing out the gel with the benzene vapour. Instead of the hysteresis loops of Anderson, fig. 62, they obtained the smooth typical sorption isotherms of fig. 63.¹ Because in parallel

¹ B. Lambert and A. M. Clark, *Proc. Roy. Soc. (London), A*, 1929, **122**, 511, fig. 2.

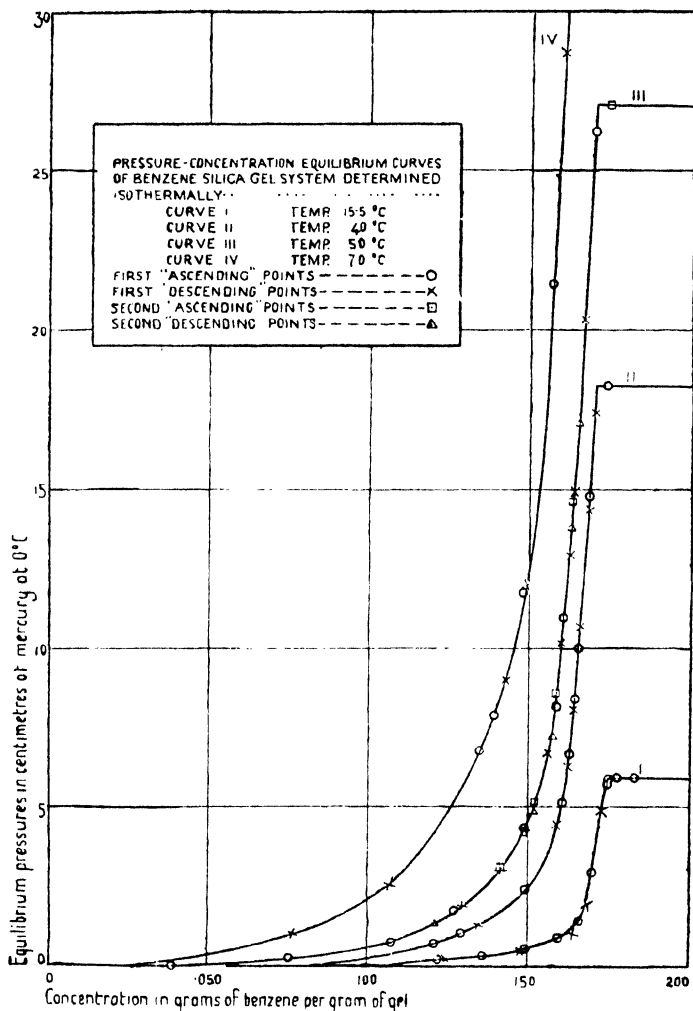


Fig. 63.—Isotherms for the Sorption of Benzene by Silica Gel (Lambert and Clark).

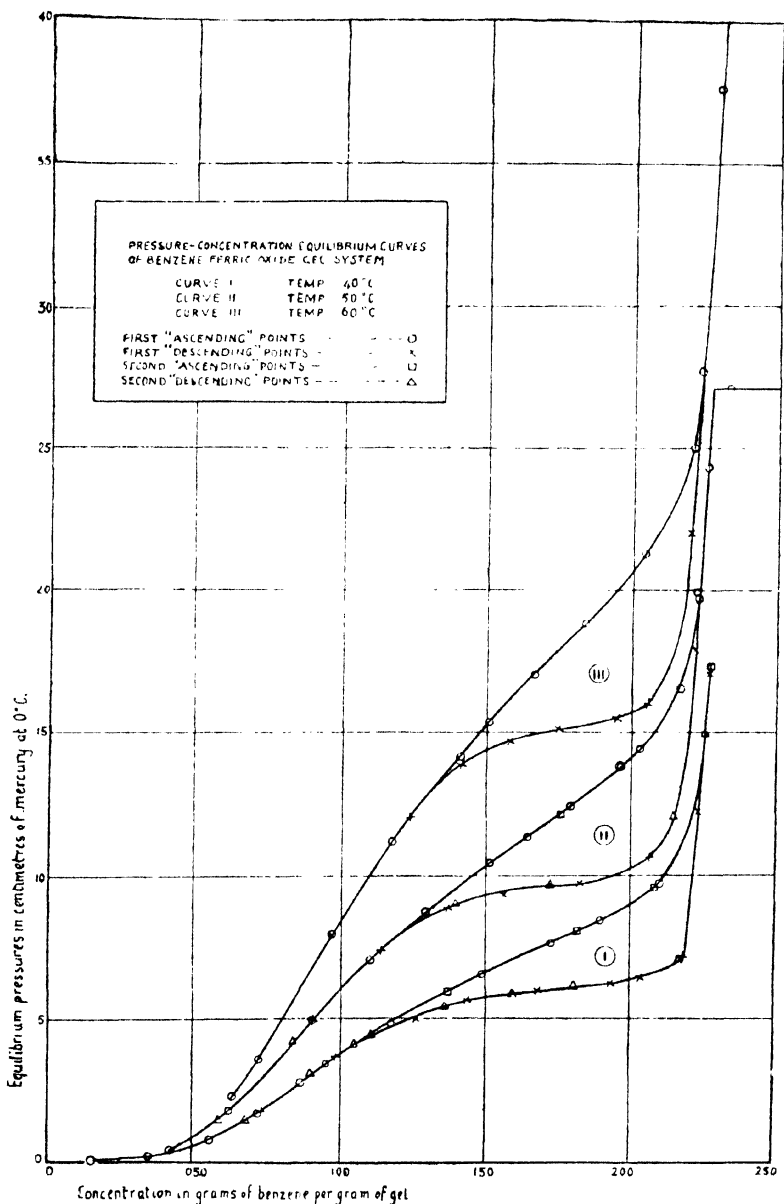


Fig. 64.—Isotherms for the Sorption of Benzene by Ferric Hydroxide Gel (Lambert and Clark).

experiments with ferric hydroxide gel they obtained the hysteresis loops shown in fig. 64,¹ they conclude, perhaps unnecessarily, that there is "a profound difference between the adsorptive properties of the analogous ferric hydroxide and silica gels".

ISOTHERMS WITH SILICA GEL AND OTHER MATERIALS

The influence of previous heating of silica gel upon its

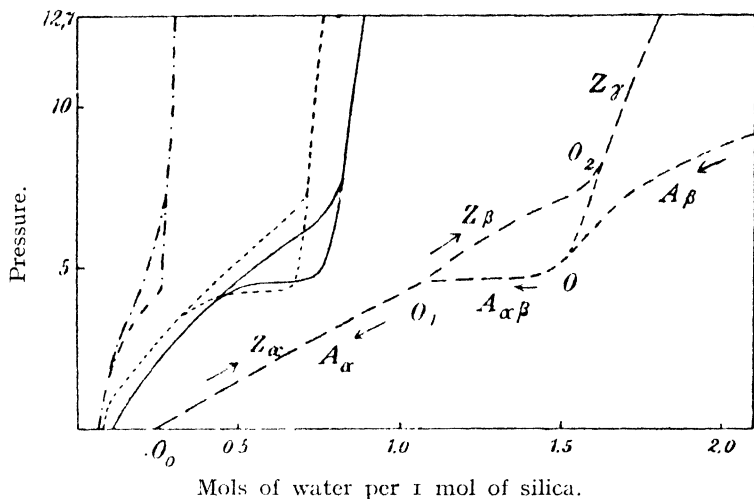


Fig. 65.—Influence of previous Heating of Silica Gel upon its Isotherms with Water.

----- fresh gel; — heated; - - - - reheated;
 ····· ignited for 10 minutes after dehydration.

isotherms with water is shown in fig. 65,² and of ageing, up to geological periods, in fig. 66.³ The effect in both cases is to

¹ B. Lambert and A. M. Clark, *Proc. Roy. Soc. (London)*, A, 1929, **122**, 507, fig. 1; see also J. C. Philip, *Trans. Inst. Chem. Eng. (London)*, 1929, **7**, 72.

² J. M. van Bemmelen, *Die Absorption*, p. 258, fig. 15.

³ After W. Bachmann, *Z. anorg. allgem. Chem.*, 1917, **100**, 41, fig. 15; adapted from J. M. van Bemmelen, *Die Absorption*, p. 225, fig. 5. See also G. Tammann's isotherms for opal and hyalite, *Z. physik. Chem.*, 1899, **27**, 333. R. Schwarz and F. Stöwener (*Kolloidchem.*

displace the curves to the left so that the pores are larger and more open, but the hysteresis loop tends finally to disappear, and the silica holds water less tenaciously except, perhaps, in the initial portion of the sorption curve. It is worth noting, on the other hand, that silicic acid jellies dissolve in water when heated below the critical temperature.

van Bemmelen's studies¹ of the isotherms and hysteresis obtained with water vapour extend to alumina, stannic oxide, various ferric oxides, chromic oxide, manganese dioxide,

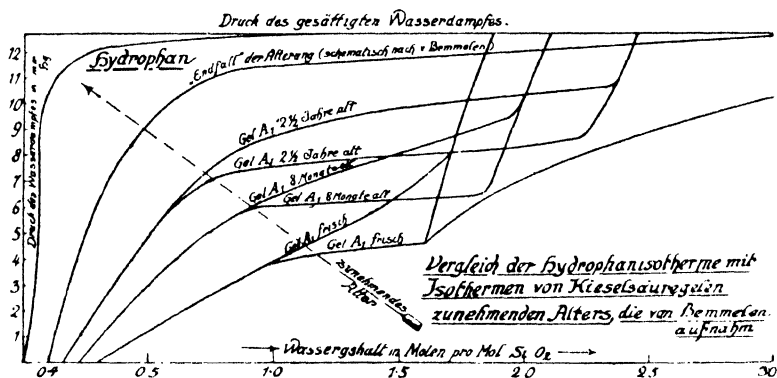


Fig. 66.— Influence of Ageing of Silica Gel upon its Isotherms with Water.

copper oxide, zirconic acid and kaolin.² Bachmann³ has obtained hysteresis curves in his comprehensive studies of

Beihefte, 1924, **19**, 171) study the ageing by a conductivity method and show the retardation thereof by admixed electrolytes and organic non-electrolytes; sorption of methylene blue is not much affected by age.

¹ Mostly reprinted with author and subject index in J. M. van Bemmelen, *Die Absorption* (1910). J. M. van Bemmelen, *Rec. trav. chim.*, 1888, **7**, 37; *J. prakt. Chem.*, N. F., 1892, **46**, 497; *Z. anorg. Chem.*, 1893, **5**, 446; 1896, **13**, 234; 1898, **18**, 14, 98; 1899, **20**, 185; 1900, **23**, 111, 321; 1902, **32**, 265; 1903, **36**, 380; 1906, **49**, 125; 1909, **62**, 1.

² J. M. van Bemmelen, *Z. anorg. Chem.*, 1904, **42**, 314.

³ W. Bachmann, *Z. anorg. allgem. Chem.*, 1917, **100**, 1.

carbon, permutit and gelatine hardened by alcohol, the latter also using benzene vapour.

Briggs¹ points out that silica can be deactivated without losing all its porosity although losing its sorptive power; hence, clearly, that sorptive power is genuine and not due to capillary condensation in pores.² He also noticed that one apparent cubic centimetre of charcoal or silica gel liberated about 5.5 volumes of permanent gas, mostly nitrogen, upon heating from 18° to 300° C. van Bemmelen³ had found that a fresh specimen of silicic acid when dried and placed in water evolved 4.2 volumes of air or permanent gas for each supposed volume of pore space, whereas five years later only 2 volumes were evolved from the same specimen. From a practical standpoint silica rather than charcoal is often used for the sorption of air and oxygen because the product is not explosive.⁴

Others who have determined isotherms for water and various preparations of silica include Berl and Burkhardt,⁵

¹ H. Briggs, *Proc. Roy. Soc. (London)*, A, 1921, **100**, 88.

² Fused silica sorbs measurable amounts of water vapour, although negligible in comparison with silica jelly. M. Guichard, *Bull. soc. chim.* (4), 1922, **31**, 647; S. Lenher, *J. Chem. Soc.*, **1926**, 1785; S. Lenher and I. R. McHaffie, *J. Phys. Chem.*, 1927, **31**, 719; similar results for benzene, S. Lenher, *J. Chem. Soc.*, **1927**, 275. The latter excluded possible solution of water in fused silica by observing that the results were independent of time (days); the well-known permeability of fused silica to helium at temperatures above 500° C. is generally ascribed to solution. Other results for fused or precipitated silica are discussed in Chapters VII, VIII and X, such as those of T. Martini (*Phil. Mag.* (5), 1899, **47**, 329), G. J. Parks (*Phil. Mag.* (6), 1903, **5**, 517), J. R. Katz (*Proc. Acad. Sci. Amsterdam*, 1912, **15**, 445), and G. R. Paranjpe (*Proc. Asiatic Soc. Bengal*, 1919, **15**, 136).

³ J. M. van Bemmelen, *Die Absorption*, p. 340.

⁴ Thus K. Peters and K. Weil (*Z. physik. Chem.*, Abt. A, 1930, **148**, 13) use silica gel to remove radium emanation quantitatively from solution in liquid air although active charcoal sorbs the emanation even more strongly. The heavier noble gases are strongly sorbed even when the charcoal or silica gel is heavily charged with lighter gases or air.

⁵ E. Berl and H. Burkhardt, *Z. anorg. allgem. Chem.*, 1928, **171**, 102.

Patrick and Greider,¹ and Hällström.² The latter's experiments extend to kaolin, fuller's earth, kieselguhr, silica, graphite, alumina, chromic oxide, ferric oxide, magnesium oxide, copper oxide, stannic oxide, anhydrous copper sulphate, manganous oxide, and cobalt oxide.

It is clear from the evidence adduced in this chapter that practically all of the work on silica gel has been carried out in the presence of sufficient extraneous substances as to be very seriously affected and even distorted thereby. This is probably inherent in the use of silica gel, since its sorptive power depends upon the amount of water which it contains. The optimum water content lies between 5 and 8 per cent for sulphur dioxide³ and at about 2 per cent for butane.⁴

SORPTION OF GASES AND VAPOURS BY SILICA GEL.

McGavack and Patrick's isotherms for silica gel and sulphur dioxide are shown in fig. 67.⁵ The sorption is expressed in cubic centimetres at N.T.P. of gas sorbed by 1 gm. of gel. Isotherms are shown for temperatures from -54° to $+100^{\circ}$ C. They agree approximately with the classical formula.

The sorption of argon and carbon dioxide has been studied by Kälberer and Mark⁶ who found that for most specimens the isotherms were linear up to appreciable fractions of an atmosphere, in accordance with Henry's law. Their isotherms

¹ W. A. Patrick and C. E. Greider, *J. Phys. Chem.*, 1925, **29**, 1031.

² M. af Hällström, *Dissert.*, Helsingfors, 1920; quoted by B. Gustaver, *Kolloidchem. Beihefte*, 1922, **15**, 310, 331.

³ J. McGavack and W. A. Patrick, *J. Am. Chem. Soc.*, 1920, **42**, 946.

⁴ W. A. Patrick and J. S. Long, *J. Phys. Chem.*, 1925, **29**, 336.

⁵ J. McGavack and W. A. Patrick, *J. Am. Chem. Soc.*, 1920, **42**, 953, fig. 2. Other isotherms for sulphur dioxide as well as for carbon dioxide and ammonia were obtained by W. A. Patrick (*Dissert.*, Göttingen, 1914); the sorption is of the same magnitude as with charcoal. Data for fifteen gels by a dynamic method for sulphur dioxide and bromine are given by E. Bosshard and E. Jaag, *Helv. Chim. Acta*, 1929, **12**, 105.

⁶ W. Kälberer and H. Mark, *Z. physik. Chem.*, Abt. A, 1928, **139**, 151; also A. Magnus and W. Kälberer, *Z. anorg. allgem. Chem.*, 1927, **164**, 357.

for argon are given in fig. 68¹; it is stated that these isotherms remained linear up to one atmosphere pressure. The sorption² of argon or nitrogen at 0°C. is about 0.1×10^{-6} mols per 1 mm. pressure; that for carbon dioxide or ethylene

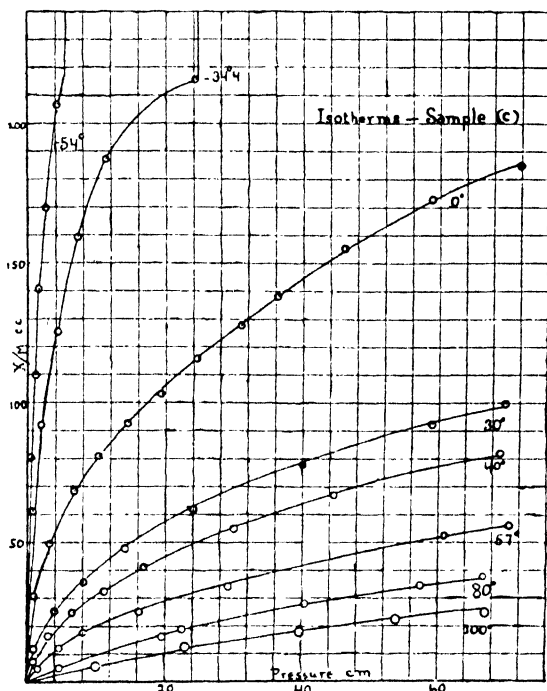


Fig. 67.—Isotherms for the Sorption of Sulphur Dioxide by Silica Gel (McGavack and Patrick).

is of the order of 1×10^{-5} . The sorption of oxygen per gram of silica gel is 0.6, 0.4 and 0.3×10^{-6} mols per mm. of pressure at 204.0°, 214.2° and 222.4° abs., respectively.³

¹ W. Kälberer and H. Mark, *Z. physik. Chem.*, Abt. A, 1928, **139**, 153, fig. 1.

² W. Kälberer and C. Schuster, *Z. physik. Chem.*, Abt. A, 1929, **141**, 274 (discrepancy between their fig. 1 and their tables 1 and 2).

³ A. Magnus and K. Grähling, *Z. physik. Chem.*, Abt. A, 1929, **145**, 27; also sorption and rate of decomposition of ozone.

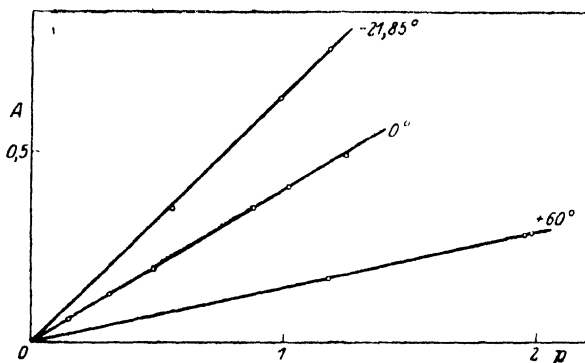


Fig. 68.—Kälberer and Mark's Isotherms for the Sorption of Argon by Silicic Acid; p in mm. Hg, A in c.c. sorbed per 188 g. of silicic acid.

The corresponding isotherms of Patrick, Preston and Owens¹ for carbon dioxide and nitrous oxide with silica gel are given

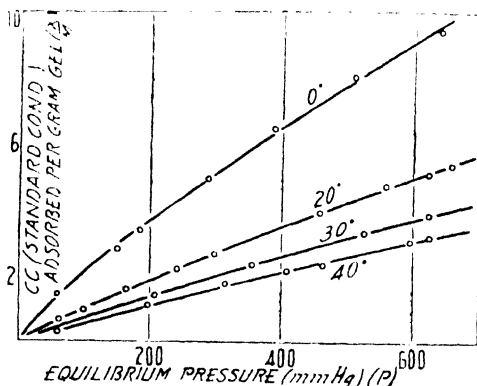


Fig. 69.—Isotherms for the Sorption of Carbon Dioxide by Silica Gel (Patrick, Preston and Owens).

¹ W. A. Patrick, W. C. Preston, and A. E. Owens, *J. Phys. Chem.*, 1925, **29**, 424. For other measurements with oxides of nitrogen see L. Cambi and L. Szegoe, *Giorn. chim. ind. applicata*, 1927, **9**, 3, and A. V. Sapozhnikov, A. P. Okatov, and M. A. Susarov, *J. Russ. Phys.-Chem. Soc.*, 1929, **61**, 1353.

in figs. 69¹ and 70.² Those for butane are reproduced in fig. 71.³ All these isotherms bear out the statement already made that the retentivity of silica gel is low as compared with charcoal even when they are alike in capacity. With charcoal far more of the sorption takes place at low pressures.

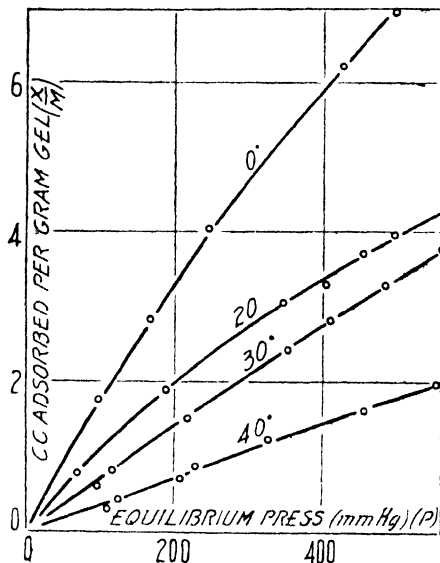


Fig. 70.—Isotherms for the Sorption of Nitrous Oxide by Silica Gel (Patrick, Preston and Owens).

This may well be due to the extraneous material and impurities in the silica gel.

Ammonia⁴ is more strongly sorbed by silica gel, which

¹ W. A. Patrick, W. C. Preston, and A. E. Owens, *J. Phys. Chem.*, 1925, **29**, 424, fig. 1.

² W. A. Patrick, W. C. Preston, and A. E. Owens, *J. Phys. Chem.*, 1925, **29**, 425, fig. 2.

³ W. A. Patrick and J. S. Long, *J. Phys. Chem.*, 1925, **29**, 337, fig. 1. For other measurements of the sorption of hydrocarbon vapours by silica gel, alumina, clay and artificial aluminium silicate, see H. Isobe, *Bull. Inst. Phys. Chem. Res. (Tokyo)*, 1930, **9**, 211.

⁴ L. Y. Davidheiser and W. A. Patrick, *J. Am. Chem. Soc.*, 1922, **44**, 1; W. Biltz and E. Rahlfs, *Z. anorg. allgem. Chem.*, 1928, **172**, 273.

Davidheiser and Patrick ascribe partly to the water and acid in the gel. The same preferential sorption of ammonia rather than carbon dioxide is shown by alumina, ferric oxide and chromic oxide.¹

Carbon dioxide, according to Magnus and Kieffer,² may be sorbed and desorbed forty times by a well-evacuated silica gel containing 5.4 per cent of water without altering the water content or sorptive behaviour of the gel. The amount

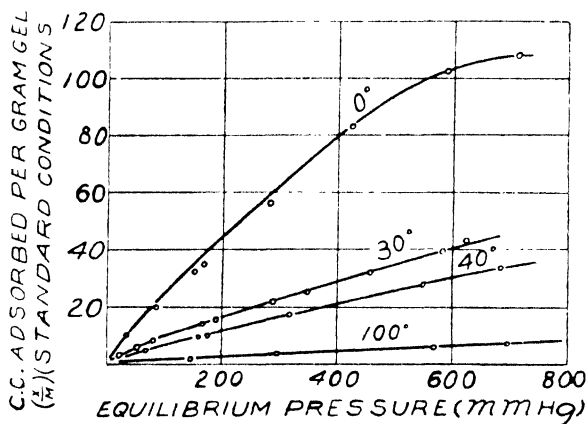


Fig. 71.—Isotherms for the Sorption of Butane by Silica Gel (Patrick and Long).

of sorption and the degree to which the sorption is proportional to the pressure is seen from the summary in table 34 on the opposite page.

Upon reducing the amount of water to 0.9 per cent, the value of A/p at 25° C. fell to 6.8; and with two other gels from silicon tetrachloride containing 2.2 and 1.1 per cent of water, this value became 25 and 20.4, respectively. Since Henry's law still held, Magnus and Kieffer ascribed the change in sorption solely to diminution of surface.

¹ N. Nikitin, *Z. anorg. allgem. Chem.*, 1926, **155**, 358.

² A. Magnus and R. Kieffer, *Z. anorg. allgem. Chem.*, 1929, **179**, 215; A. Magnus and H. Giebenhain, *Z. physik. Chem.*, Abt. A, 1929, **143**, 265.

TABLE 34

Sorption of Carbon Dioxide in Micromols (A in mols $\times 10^{-6}$) per 55 g. of Silica Gel containing 5.4 per cent of Water, at various Temperatures and Pressures (p in mm. of Hg)

Temperature	— 21.2° C.	— 11° C.	0° C.	25° C.	50° C.	100° C
A/p at lower pressures .	1,239	698	400*	134	56.5	16.5
A/p for $p = 400$ mm. .	—	—	180	94	47	16.3

* $x/m = 0.000320$ g. of carbon dioxide per 1 gm. of silica gel for $A = 400 \times 10^{-6}$ mols per 55 g. silica gel.

On the other hand, ammonia (or chlorine) carries off water with it when it is desorbed. Hence the data are irregular. Henry's law holds for sorption (without desorption) up to 1500×10^{-6} mols per 1 gm. of gel, the pressure being 0.02 mm. at 50° C. The ammonia replaces the water of the gel. Hence the heat evolved may be several times as great as the "true heat of sorption" which in itself is half as great again as the heat of solution of ammonia in water. Magnus and Kieffer deduced this true heat of sorption from experiments with silica gels that had been further dehydrated; for 1.2 per cent water the observed heat was reduced to half that for 5.4 per cent water. The sorption isotherms are much more strongly curved than with carbon dioxide. The latter reacts with any oxide or hydroxide formed by hydrolysis in preparing precipitates of calcium or barium fluoride, or barium sulphate; and chemical action was suspected in Magnus and Kieffer's experiments with titania and zirconia. For chlorine,¹ the isotherms are likewise curved for sorption exceeding 18×10^{-6} mols per gram of silica gel containing 1.63 per cent water; the initial sorption by one gram per millimetre pressure is 13.6, 5.60 and 2.62×10^{-6} mols at 0°, 20° and 40° C., respectively.

Others who have measured the sorption of various vapours by silica gels of different origins, chiefly using dynamic

¹ A. Magnus and A. Müller, *Z. physik. Chem.*, Abt. A, 1930, **148**, 251.

methods, are Holmes and Weide,¹ Patrick and Opdycke,² Okatov,³ Jones and Outridge,⁴ von Putnoký and von Szelenyi,⁵ Traube and Birutowitsch,⁶ Berl and Wachendorff,⁷ Alekseevski,⁸ and Ray.⁹

The sorption of binary mixtures of carbon monoxide, carbon dioxide and oxygen by silica has been shown by Markham and Benton¹⁰ to be calculable from an extension of the Langmuir formula.

OTHER POROUS OXIDES

It is interesting to compare the sorptive powers of other oxides with that of silica gel. Nikitin's graphs¹¹ may be

¹ H. N. Holmes and H. F. Weide, *Science*, 1924, **60**, 596 (benzene, toluene, acetone, methyl alcohol, ethyl alcohol, acetic acid, methyl propionate and ethyl acetate).

² W. A. Patrick and L. H. Opdycke, *J. Phys. Chem.*, 1925, **29**, 601 (alcohol, carbon tetrachloride, benzene and water).

³ A. P. Okatov, *Zhur. Prikladnoi Khim.*, 1929, **2**, 21 (benzene, ether, alcohol and water by charcoal and silica gels).

⁴ D. C. Jones and L. Outridge, *J. Chem. Soc.*, 1930, 1574 (mixtures of *n*-butyl alcohol and benzene vapours).

⁵ L. von Putnoký and G. von Szelenyi, *Z. Elektrochem.*, 1928, **34**, 805; 1930, **36**, 10 (alcohol and ether and their mixtures by six different silica gels).

⁶ J. Traube and St. Birutowitsch, *Kolloid-Z.*, 1928, **44**, 233 (methyl acetate, acetone, benzene and methyl ethyl ketone by silica gel; and water, carbon disulphide, methyl acetate, acetone, methyl alcohol, hexane, ethyl acetate, ethyl alcohol, benzene, methyl ethyl ketone, propyl alcohol, iso-amyl alcohol by charcoal; also sorption velocity).

⁷ E. Berl and E. Wachendorff, *Z. angew. Chem.*, 1924, **37**, 747 (benzene by silica and five varieties of active carbon, including rate).

⁸ E. V. Alekseevski, *J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 403 (acetylene, ethylene, iso-butylene, alcohol and benzene by catalysts such as floridin (a variety of bleaching or fuller's earth), alumina, powdered glass, kaolin, etc.); 1930, **62**, 221 (for alcohols and for ethylene hydrocarbons the optimum temperature of ignition of alumina is 410°C. and 610°C., respectively).

⁹ R. C. Ray, *J. Phys. Chem.*, 1925, **29**, 74 (nitrogen peroxide by silica gel and by silica gel in which the original water is replaced by nitric acid).

¹⁰ E. C. Markham and A. F. Benton, *J. Am. Chem. Soc.*, 1931, **53**, 497.

¹¹ N. Nikitin *Z. anorg. allgem. Chem.*, 1926, **155**, 358 and 359, figs. 1, 2 and 3.

adduced for this purpose ; see figs. 72, 73 and 74 for alumina, ferric oxide and chromic oxide, respectively, where sorption is expressed in cubic centimetres at N.T.P. for about 3 g. of solid. It will be noted that the sorptive powers for ammonia fall off in the order given, the alumina at -20°C . taking up 10 per cent by weight of ammonia. For comparison it may

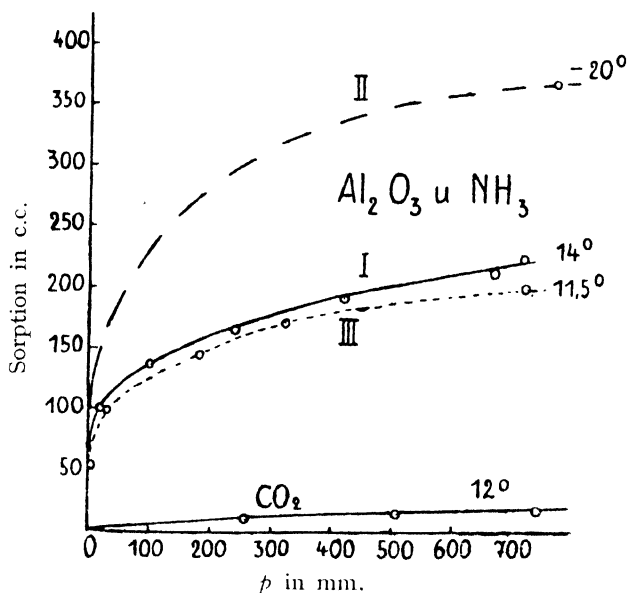


Fig. 72.—Sorption by Alumina. Graphs I and II for Ammonia and that for Carbon Dioxide refer to 3.01 g. of Alumina previously heated to 350°C . and retaining 15 per cent of Water. Graph III for Ammonia refers to the same weight of Alumina heated to 600°C . and retaining 6.7 per cent of water.

be mentioned that 1 gm. of calcium oxide sorbed only 0.7 c.c. of ammonia at 15° and 760 mm. pressure.¹

¹ M. Guichard (*Bull. soc. chim.* (4), 1910, **7**, 1017; *Compt. rend.*, 1910, **151**, 236) observed the sorption of iodine from saturated vapour by opal, agate, silica, alumina, beryllium oxide, magnesium oxide and charcoal. As the porosity of magnesium oxide becomes less through calcination, its sorptive power for iodine diminishes until it almost disappears at density 3.5.

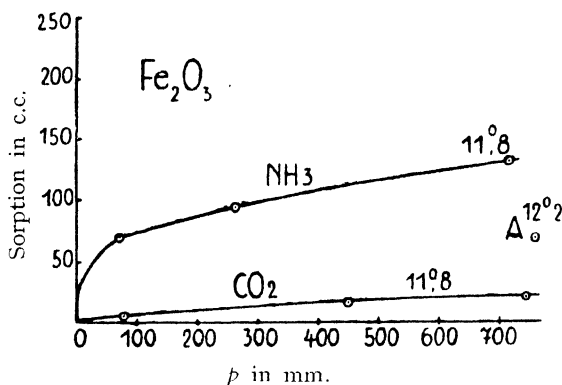


FIG. 73.—Sorption by 2.55 g. of Ferric Oxide heated to 350°C . The point marked A for ammonia was obtained after further heating to 600°C ., during which treatment it lost 1 per cent of water.¹

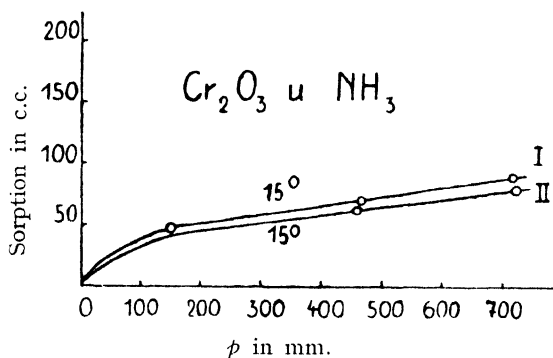


Fig. 74.—Sorption of Ammonia by 2.55 g. of Chromic Oxide. Graph I refers to Oxide heated to 250°C . and Graph II to Oxide dried at 350°C . Many days were required for the Sorption.

¹ Ferric oxide after being heated to 550°C . sorbs less than one-quarter as much water vapour as it does when it has been heated only to 300° (P. H. Emmett and K. S. Love, *J. Phys. Chem.*, 1930, **34**, 54); see also L. A. Welo and O. Baudisch (*J. Biol. Chem.*, 1925, **65**, 215) for sorption of water vapour and of oxygen.

Others who have investigated the sorbing powers of alumina are Munro and Johnson,¹ Gurwitsch,² Pearce and Alvarado,³ Perry,⁴ and Hahn and Biltz.⁵ Water is taken up to a larger extent than any other vapour.⁶ Other substances are readily removed from alumina by an air current at a temperature a few degrees above the boiling point of the vapour in accordance with the low retentivity already referred to. Some saturation values found for x/m for alumina are given in table 35. A number of vapours, such as acetone, decompose in contact with alumina.

In table 36 are given the saturation values which Perry has obtained for x/m for ferric hydroxide containing 6.36 per cent of water. The sorptive power of this ferric hydroxide was superior to that of specimens containing larger amounts of water.

¹ L. A. Munro and F. M. G. Johnson, *Ind. Eng. Chem.*, 1925, **17**, 88; *J. Phys. Chem.*, 1926, **30**, 172 (27 substances including hydrocarbons, alcohols, esters, ether, acetone, halogen derivatives, carbon dioxide, sulphur dioxide, ammonia, etc.; also water at various temperatures and pressures).

² L. G. Gurwitsch, *Z. physik. Chem.*, 1914, **87**, 323; *J. Russ. Phys.-Chem. Soc.*, 1915, **47**, 805; floridin, alumina and bone charcoal with water, carbon disulphide and numerous organic compounds of different series.

³ J. N. Pearce and A. M. Alvarado, *J. Phys. Chem.*, 1925, **29**, 256; water, ethyl alcohol, ethyl acetate and acetic acid by alumina and thoria.

⁴ J. H. Perry, *J. Phys. Chem.*, 1925, **29**, 1462 (ten vapours). W. Müller-Erbach (*Repertorium der Physik*, 1885, **21**, 407; *Verhandl. physik. Ges. Berlin*, 1885, Nos. 1 and 4) measured the sorption of water and carbon disulphide and their mixtures by ferric oxide and alumina and calculated the thickness of the sorbed layer upon the assumption that they were not porous.

⁵ O. Hahn and M. Biltz, *Z. physik. Chem.*, 1927, **126**, 323; M. Biltz, *Z. physik. Chem.*, 1927, **126**, 356 (where previous references may be found, including O. Hahn, *Z. Elektrochem.*, 1923, **29**, 189); hydration and dehydration of the hydrous oxides, ferric oxide, thoria, zirconia and alumina; also sorption of thorium emanation and radium emanation.

⁶ L. H. Milligan (*J. Phys. Chem.*, 1922, **26**, 247) found that porous alumina takes up more water the lower the temperature of ignition, the X-ray pattern not changing during the sorption.

TABLE 35

Saturation Values of x/m for various Vapours Sorbed by Alumina

Vapour	x/m	Vapour	x/m
Chloroform	0.38	Toluene	0.28
Dichlorethane	0.37	Acetic acid	0.27
Carbon tetrachloride	0.36	Methyl acetate	0.26
Dichlorethylene	0.34	Hexane	0.25
Carbon disulphide	0.30	Methyl ethyl ketone	0.25

TABLE 36

Saturation Values of x/m for various Gases and Vapours Sorbed by Ferric Hydroxide containing 6.36 per cent of Water

Substance	x/m	Substance	x/m
Acetone	0.51	Ethyl bromide	0.12
Chloroform	0.36	Alcohol	0.11
Carbon tetrachloride	0.33	Sulphur dioxide in presence	
Butyl alcohol	0.29	of air	0.11
Dichlorethylene	0.28	Benzene	0.10
Iso-butyl alcohol	0.21	Methyl alcohol	0.10
Methyl iodide	0.13	Gasoline	0.067
Sulphur dioxide	0.13	Ammonia	0.044
		Ammonia in presence of air	0.035

Chowdhury and Pal¹ measured the sorption of benzene by mixed oxides of iron, aluminium and silicon and found that the two component adsorbents were always superior to either component alone.

Titania jelly or gel was found by Klosky² to be less sorptive than silica gel for sulphur dioxide, chlorine, butane, methyl chloride and ammonia. By a dynamic method Klosky and Burggraff³ found the highest values for x/m in grams per gram for sulphur dioxide to be 0.3, 0.2, 0.08 and 0.07 at -22.5° , 0° , 25° and 50° C., respectively. The sorption of carbon dioxide, hydrogen, ethylene and ethane by titania catalysts was observed by Bischoff and Adkins.⁴

¹ J. K. Chowdhury and M. N. Pal, *J. Indian Chem. Soc.*, 1930, **7**, 451.

² S. Klosky, *J. Phys. Chem.*, 1930, **34**, 2622; S. Klosky and C. Marzano, *J. Phys. Chem.*, 1925, **29**, 1125; S. Klosky and L. P. L. Woo, *J. Phys. Chem.*, 1928, **32**, 1387.

³ S. Klosky and A. J. Burggraff, *J. Am. Chem. Soc.*, 1928, **50**, 1045.

⁴ F. Bischoff and H. Adkins, *J. Am. Chem. Soc.*, 1925, **47**, 823.

Stannic oxide gel has about one-fourth the sorbing capacity of titania gel for ammonia.¹ Thus at one atmosphere at room temperature, titania sorbed the following amounts of various vapours :

Vapour	. C_6H_6 .	$(CH_3)_2CO$	NH_3	$CHCl_3$	CH_3COOH	CS_2
x/m in grams/ gram	. 0.32	0.30	0.085	0.55	0.43	0.43
Vapour	. $(CH_3CO)_2O$	C_5H_5N	$C_6H_4(CH_3)_2$	$CH_3 \cdot C_6H_4 \cdot OH$	$(C_2H_5)_2O$	
x/m in grams/ gram	. 0.37	0.36	0.30	0.038	0.27	

Ceria and thoria are likewise far poorer sorbents than titania.

The sorption isotherms for stannous oxide obtained by Pearce and Miss Goergen are shown in fig. 75.² Acetylene is polymerized above $100^\circ C$. and the oxide is reduced by hydrogen above $183^\circ C$.

Thoria³ sorbs nitrogen and hydrogen in proportion to the pressure, the amount sorbed at 1 atmosphere by 1 gm. of thoria being only 0.015 c.c. (at N.T.P.) for hydrogen at $0^\circ C$. or nitrogen at $100^\circ C$. The isotherm for ethylene at $0^\circ C$. is much curved, tending towards the total of about 4.5 c.c. (at N.T.P.) per gram of thoria. The isotherm for alcohol included much lower values and exhibited a complicated form.

Pearce and his collaborators⁴ obtained smooth isotherms with thoria and other oxides. Figs. 76⁵ and 77⁶ are given as an instructive comparison of the relative sorbing powers of thoria, alumina, tungstic oxide and zirconia, the order being exactly the reverse with water from that observed with alcohol and ethyl acetate, and, with one exception, acetic acid.

¹ N. I. Nikitin and V. I. Yuryev, *Z. anorg. allgem. Chem.*, 1928, **171**, 281; *J. Russ. Phys.-Chem. Soc.*, 1929, **61**, 1029.

² J. N. Pearce and S. M. Goergen, *J. Phys. Chem.*, 1928, **32**, 1431, fig. 3.

³ G. I. Hoover and E. K. Rideal, *J. Am. Chem. Soc.*, 1927, **49**, 118.

⁴ J. N. Pearce and M. J. Rice, *J. Phys. Chem.*, 1929, **33**, 692; J. N. Pearce and A. M. Alvarado, *J. Phys. Chem.*, 1925, **29**, 256.

⁵ J. N. Pearce and M. J. Rice, *J. Phys. Chem.*, 1929, **33**, 698, fig. 1.

⁶ J. N. Pearce and M. J. Rice, *J. Phys. Chem.*, 1929, **33**, 699, fig. 2.

Many measurements by Lazier and Adkins ¹ are summarized in table 37, showing the number of cubic centimetres (at

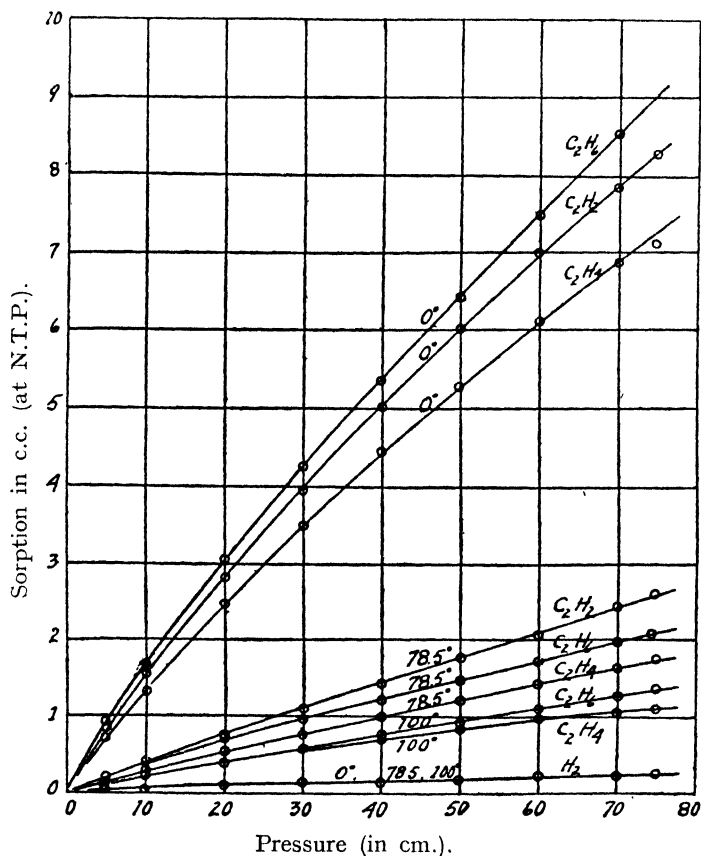


Fig. 75.—Volumes in c.c. (at N.T.P.) of Hydrogen, Acetylene, Ethylene and Ethane Sorbed by 10 g. of Stannous Oxide at 0° , 78.5° and 100° C.

22° C. and 740 mm. pressure) sorbed by 1 gm. of catalyst ; the iron oxide sorbed 0.65 c.c. of carbon monoxide.

¹ W. A. Lazier and H. Adkins, *J. Phys. Chem.*, 1926, **30**, 356.

TABLE 37

Volumes in c.c. (at 22° C. and 740 mm. pressure) of Ethylene and Hydrogen Sorbed by 1 gm. of various Catalysts

Catalyst	Ethylene	Hydrogen
Copper (Merck)	0.072	0.24
Copper (ex nitrate)	0.020	0.0055
Nickel (by hydrogen)	0.70	0.84
Nickel (by alcohol)	2.05	0.61
Zinc oxide (ex hydroxide)	0.57	0.018
Zinc oxide (ex isopropoxide)	1.67	0.234
Iron oxide (precipitated)	5.88	0.000

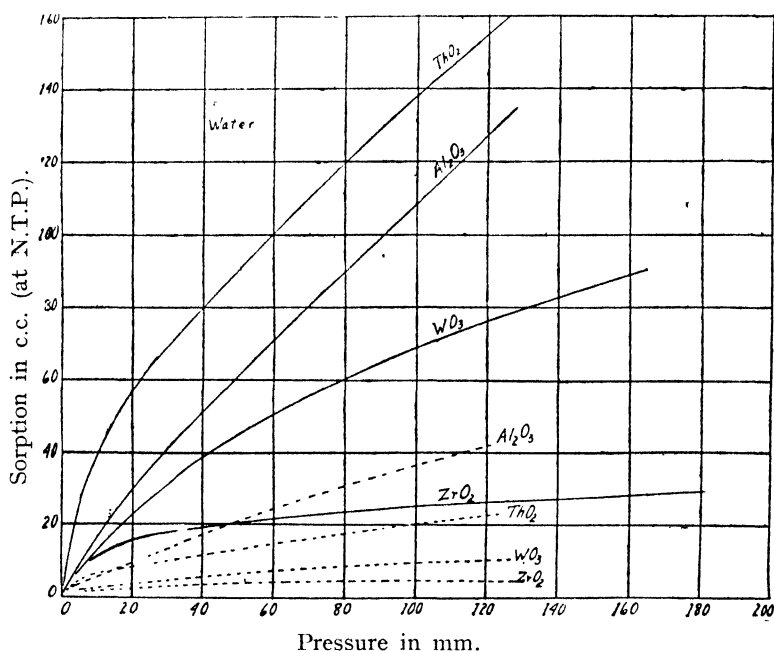


Fig. 76.—Volumes in c.c. (at N.T.P.) of Water Vapour Sorbed by 1 g. of Oxide at 99.4° C. (dotted curves); and (full curves) c.c. (at N.T.P.) sorbed by 1 (bulk) c.c. of Oxide.

Zinc oxide was shown *not* to sorb either hydrogen or carbon monoxide after evacuation at 300° C.; but between 300° and 400° C. a rapid evolution of sorbed water and carbon dioxide occurred, after which the oxide was able to sorb hydrogen

or carbon monoxide.¹ However, their removal was always accompanied by some reduction to metal.² Typical sorptions observed were 0.50 c.c. (at N.T.P.) of hydrogen by 1 gm. of zinc oxide at 0° C. and 20 mm. pressure, with a much

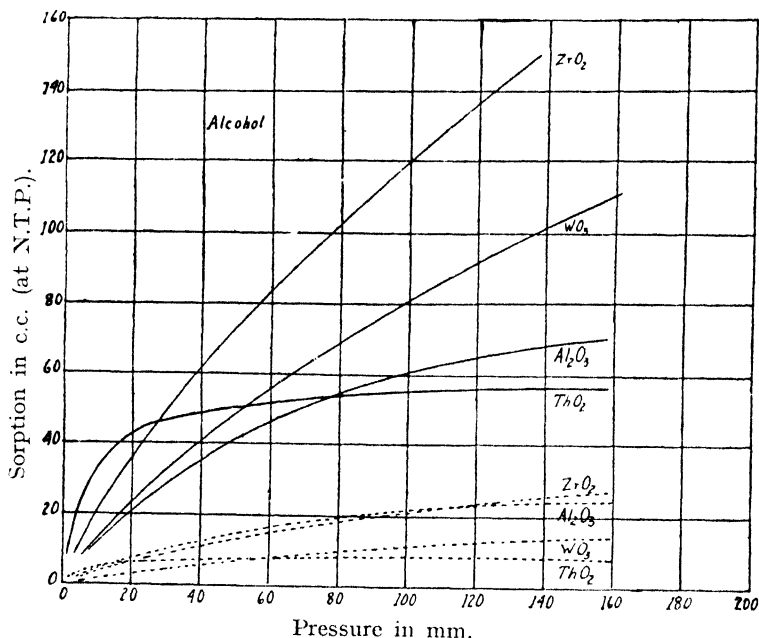


Fig. 77.—Volumes in c.c. (at N.T.P.) of Alcohol Vapour Sorbed by 1 g. of Oxide at 99.4° C. (dotted curves); and (full curves) c.c. (at N.T.P.) sorbed by 1 (bulk) c.c. of Oxide.

greater value for carbon dioxide; and 1.84 c.c. of hydrogen at 100° C. and 1 mm. pressure by a catalyst containing about two mols of zinc oxide to one of chromic oxide. These values

¹ H. S. Taylor and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, 1927, **49**, 2471.

² E. W. Flösdorf and G. B. Kistiakowsky (*J. Phys. Chem.*, 1930, **34**, 1908) subsequently found that not until the zinc-chromium oxide had been thoroughly treated with hydrogen at 300° C. was a reversible and strong sorbent for hydrogen obtained, stronger at 0° than at 100° C.

very greatly exceed the sorptions observed with the best nickel and even copper catalysts.

The oxides of copper and manganese have received much attention on account of their importance as catalytic oxidants of carbon monoxide, a gas which is not strongly enough sorbed for the usual gas mask to afford protection. The most extensive sorption data are those of Benton,¹ an excerpt from whose measurements is given in table 38, which also includes data for precipitated silica and other oxides. Measurements were also made at -79°C. , $+25^{\circ}\text{C.}$ and 184°C.

TABLE 38

Volumes in Cubic Centimetres at N.T.P. Sorbed at 1 Atmosphere Pressure by 1 gm. of various Oxides dried at 200°C.

*(Except CuO, 400°C. and V_2O_5 , 250°C.)**

At 0°C.							
Gas	V_2O_5	CuO	Hopcalite †	MnO_2	Co_2O_3	Fe_2O_3	SiO_2
CO_2 . . .	0.376	4.53	6.18 .	8.66	10.21	17.79	33.32
O_2 . . .	0.031	0.128	0.247	0.34	0.264	0.484	1.507
H_2 . . .	0.000	0.085	0.08	0.11	—	0.089	0.234
CO . . .	0.053	1.66	4.42	1.90	—	1.62	2.262
At 110°C.							
CO_2 . . .	0.051	0.50	0.70	1.20	2.46	2.92	3.13
O_2 . . .	0.015	0.037	0.064	0.085	0.073	0.123	0.306

* According to T. Carnelley and J. Walker (*J. Chem. Soc.*, 1888, 53, 59) the oxides so prepared should have the following composition: $5\text{SiO}_2 \cdot \text{H}_2\text{O}$; $2\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$; and $4\text{Co}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

† 60% MnO_2 + 40% CuO, bulk density 0.45.

The dead space in Benton's apparatus was measured by means of helium. Manganese dioxide was shown to sorb 0.301, 0.081, and 0.038 c.c. (at N.T.P.) of nitrogen at 25°C. , 110°C. , and 184°C. , respectively. Comparison of the time curves for helium and nitrogen with those of oxygen and carbon dioxide led to the inference that some of the last two gases were dissolved by the oxides.² Some of the hydro-

¹ A. F. Benton, *J. Am. Chem. Soc.*, 1923, 45, 887, 902.

² Oxygen can diffuse through metallic oxides at comparatively low temperatures. See P. Schutzenberger, *Compt. rend.*, 1884, 98, 1520; T. W. Richards and E. F. Rogers, *Am. Chem. J.*, 1893, 15, 567.

gen and more of the carbon monoxide must have been oxidized.

Isotherms of the form usual with charcoal have been found by Lanning¹ for various samples of manganese dioxide. The amounts of carbon dioxide sorbed are of a lower order of magnitude than the total amount of water which can be taken up at high relative humidities. Water interferes with the sorption of carbon dioxide.² The isotherms of Bray and Draper³ for water with copper oxide are reproduced in Chapter XVI, page 443, fig. 133. At low relative humidities an ordinary sorption curve is obtained, but as the relative humidity increases, far greater amounts of water are taken up, obviously by condensation of water in bulk in the rather coarse pores. Similar isotherms for the sorption of water by manganese dioxide have been obtained by Foote and Dixon⁴ and by Lanning.⁵ No hysteresis was observed.

PRACTICAL SIGNIFICANCE OF HUMIDITY CHANGES

The phenomena described in this chapter might appear to be of merely academic interest with perhaps a few applications to contact catalysis and to soil chemistry. It is therefore of interest to point out the significance of such studies in so important a phase of practical life as the specification of materials for public and private buildings designed for permanence. It has been shown that in European climates, of all the causes of fluctuating strains in building materials, varying humidity exceeds in importance any other factor by at least fivefold. In an investigation carried out for the Building Research Station of the Department of Scientific and Industrial Research of Great Britain, McBain and

¹ C. E. Lanning, *J. Am. Chem. Soc.*, 1930, **52**, 2414.

² H. W. Foote and J. K. Dixon, *J. Am. Chem. Soc.*, 1931, **53**, 55.

³ W. C. Bray and H. D. Draper, *Proc. Nat. Acad. Sciences*, 1926, **12**, 295; J. A. Almquist and W. C. Bray, *J. Am. Chem. Soc.*, 1923, **45**, 2305; H. D. Draper, *J. Am. Chem. Soc.*, 1928, **50**, 2637.

⁴ H. W. Foote and J. K. Dixon, *J. Am. Chem. Soc.*, 1930, **52**, 2174; also isotherms for benzene.

⁵ C. E. Lanning, *J. Am. Chem. Soc.*, 1930, **52**, 2413.

Ferguson¹ were able to show that the intergrain cement of sandstones, for example, is of the rigid, porous type dealt with in this chapter. Certain other building stones, such as pure limestone, are exempt from disintegrating action due to this particular cause. Well-burnt bricks of good quality, although coarsely porous, do not sorb appreciable amounts of water. Taken in conjunction with the fact discovered by Meehan² in an *ad hoc* experiment that these rigid gels, like charcoal, swell and shrink measurably during sorption and desorption, it is evident that "a definite step forward has been made in the understanding of the fundamental properties of such materials as sandstones, concretes, plasters, etc."³

¹ J. W. McBain and J. Ferguson, *J. Phys. Chem.*, 1927, **31**, 564 (isotherms with water for powdered quartz, sand, fibres of fused silica, kieselguhr and "filter cel", sandstones, limestones, chalk, bricks, and granite; also isotherms with benzene, octane, chloroform, methyl alcohol, and ethyl alcohol by sandstones and their intergrain cement).

² F. T. Meehan, *Proc. Roy. Soc. (London)*, A, 1927, **115**, 199.

³ *Report of the Building Research Board for the period ended 31st December, 1926.* H.M. Stationery Office, London, 1926.

CHAPTER VII

SORPTION BY GLASS

The literature upon sorption by glass is extensive because glass is such a common laboratory material and on account of its technical importance in electric lighting and the manufacture of vacuum tubes.

THE UNIVERSAL CORROSION OF GLASS SURFACES

From a theoretical standpoint, however, the data are not easily interpreted. Every chemist since Scheele and Lavoisier knows that water extracts alkali, as well as some silicate, from glass¹ so that, for example, water which has been boiled in a vessel of soft glass will colour phenolphthalein a bright red. Glass, when finely pulverized, yields alkali even to cold water.² Glass owes its power of resisting agents generally to the existence of an insoluble film of silica or highly silicated matter upon its surface.² The silica is mostly left behind as a coating of silica gel upon the surface of the glass.³ This is amplified when the usual corrosive cleaning agents are employed. Surfaces so prepared for use are no longer glass, and they possess appreciable depth and porosity in the sense used in the preceding chapter. Such "cleansing", if carried too far, renders glass wool so brittle that it may fall to powder. The frequent use of glass wool or glass powder with the object of obtaining a large surface introduces the further uncertainty that it provides numerous capillary spaces in which vapours

¹ For some numerical details and references see E. Warburg and T. Ihmori, *Wied. Ann. der Physik.*, 1886, **27**, 489.

² M. Faraday, *Phil. Trans. Roy. Soc. London*, 1830, Part I, p. 49.

³ "Moteless water shaken in ordinary 'clean' glass apparatus rapidly acquires many motes" (A. W. C. Menzies, *Nature*, 1930, **125**, 445).

at high relative humidity can condense in bulk. Few of the authors who have worked with powders have considered that this was a source of serious error, but their work, for this reason, has not met with general acceptance.

The optical polishing of glass surfaces is known to produce innumerable minute cracks, and the chemical uncertainties¹ which accompany it (apart from frequent embedding of rouge) are indicated in the following abstract of a paper by Preston.²

"The attrition of the iron grinding blocks liberates H_2 from the water during the grinding and polishing of plate glass. The glass removed by the rouge is attacked by the water. Gelatinous SiO_2 is precipitated with $Fe(OH)_2$ and $Fe(OH)_3$ in the presence of $FeSO_4$, hardening during the operation. Na_2SO_4 also forms and appears in hairy growths of acicular crystals upon slow drying."

PERMEABILITY OF GLASS AND SOLUBILITY THEREIN

Furthermore, glass is permeable to helium at all temperatures and to hydrogen and other gases at high temperatures.³ Paneth and Peters show that at room temperature and 0.5 atmosphere pressure about 10^{-11} c.c. of helium passes

¹ Scheringa (*Ber. u. Mitt. über d. staatl. Gesundheitsfürs.*, 1922, Nr. 7, p. 641; *Physik. Ber.*, 1923, **4**, 118) warns that sand, owing to organic impurities, has a strong affinity for water vapour. Only by boiling out with a strong oxidizing agent, or by heating to redness, can a white, non-hygroscopic product be obtained.

² F. W. Preston, *J. Soc. Glass Tech.*, 1930, **14**, 127T.

³ For references and data for hydrogen, helium and nitrogen, using Pyrex, Jena glass, and fused silica, see G. A. Williams and J. B. Ferguson, *J. Am. Chem. Soc.*, 1922, **44**, 2160. See also H. Le Chatelier, *La Silice et les Silicates*, p. 93 (A. Hermann et Fils, Paris, 1914); E. C. Mayer, *Phys. Rev.*, (2), 1915, **6**, 283; A. Sieverts and E. Bergner (*Ber.*, 1912, **45**, 2576) found that 6.7 g. of powdered fused silica sorbs 0.1 c.c. of helium or hydrogen at $1,100^\circ C.$, diffusing freely through it; for hydrogen in fused silica, see M. W. Travers, L. E. Hockin and T. J. P. Pearce, *Nature*, 1931, **128**, 66. C. Zenghelis (*Z. physik. Chem.*, 1909, **65**, 341) alleged that glass was permeable to halogen vapours; this was controverted by A. Stock and H. Heynemann (*Ber.*, 1909, **42**, 1800), H. Landolt (*Z. physik. Chem.*, 1909, **68**, 169), A. V. Elsdon (*Proc. Chem. Soc.*, 1910, **26**, 7), B. Tollens (*Ber.*, 1909, **42**, 2013), and J. B. Firth (*Proc. Chem. Soc.*, 1913, **29**, 111); but partially reaffirmed for certain specimens of glass by C. Zenghelis (*Z. physik. Chem.*, 1910, **72**, 425).

per hour through 1 sq. cm. of glass wall 5 mm. thick. The helium in the atmosphere will accumulate in an empty vessel by mere diffusion through the glass walls. Glass sorbs helium far more strongly than neon so that pure helium is readily obtainable by fractional sorption. 10,000 sq. cm. of glass tubing sorb between 10^{-3} and 10^{-4} c.c.¹

Water and carbon dioxide penetrate into glass even at room temperature and, if they have not been baked out, they gradually spoil the vacuum in a glass tube or vessel. Water under high pressures passes freely through glass walls a centimetre or more thick. This is strikingly illustrated by the thick glass floats and other implements used in oceanography, which soon fill with water.

Mitscherlich² showed the presence of sorbed gas and moisture on the surface of glass which has not been baked out by observing the bubbles which form between it and boiled mercury upon warming. Baker³ showed by means of the following experiment that some of this water comes out of the deeper layers of the glass.

"A glass bottle was heated to about 150° C. while a current of air dried by sulphuric acid was drawn through it. When it was cool, it was filled with clean sodium amalgam. After two days bubbles of hydrogen began to appear between the glass and the amalgam, and after three days the whole of the glass was covered with bubbles. Since these did not appear in the first twelve hours, their formation could not be ascribed to surface water."

When glass which has sorbed oxygen and carbon dioxide under pressure is quickly heated to the softening point, the escape of gas causes frothing of the surface of the glass.⁴

During the process of manufacture, whilst the glass is in the liquid condition, large quantities of carbon dioxide,

¹ F. Paneth and K. Peters, *Z. physik. Chem.*, Abt. B, 1928, **1**, 253. Asbestos and palladium in contrast to glass exhibit no selective sorption for helium (see Chapter IX, page 283).

² M. E. Mitscherlich, *Taylor's Scientific Memoirs*, 1846, **4**, 7.

³ H. B. Baker, *J. Chem. Soc.*, **1929**, 1662. See also C. A. Kraus and E. H. Darby, *J. Am. Chem. Soc.*, 1922, **44**, 2783.

⁴ J. B. Hannay, *Chem. News.*, 1881, **44**, 3; *Ber.*, 1881, **14**, 2221.

oxygen, nitrogen and water vapour are evolved. On cooling, appreciable quantities of these substances remain in solution.¹ Washburn² showed that when glass is heated to 1,200° C. and suddenly exposed to a vacuum, it swells to a white mass of foam occupying many times the volume of the original glass. It was found that oxygen and carbon dioxide are present in solution to the extent of 0.1 per cent of the weight of the glass. Some glasses contained a volume of dissolved gas (oxygen, carbon dioxide and nitrogen measured at N.T.P.) between 20 and 110 per cent of the volume of the glass itself. Glass which has been heated for an hour to 1,500° or 1,600° C. retains much less gas than ordinary glass,³ and Harris and Schumacher found that 90 per cent of this gas is given up at 200° C.

When evacuated glass apparatus is sealed off, the pressure is always appreciably increased, due to the gases released when melting the glass at the constriction.⁴ "The vacuum in sealed vessels deteriorates with time, rapidly at first, and then more slowly, and subsequent heating, even at temperatures lower than the heat-treating temperature, results in increase of pressure due to further liberation of the gases and vapours from the glass."⁵ The evolution of the gas

¹ S. R. Scoles, *Glass Ind.*, 1926, **7**, 179.

² E. W. Washburn, F. F. Footitt and E. N. Bunting, Univ. of Illinois Eng. Expt. Station, 1920, Bull. No. 118 (*Univ. Illinois Bull.*, 1920, **18**, No. 15).

³ J. E. Harris and E. E. Schumacher, *Ind. Eng. Chem.*, 1923, **15**, 176.

⁴ See for example, J. E. Shrader, *Phys. Rev.*, (2), 1919, **13**, 434.

⁵ J. E. Shrader, *Phys. Rev.*, (2), 1919, **13**, 437; see also R. G. Sherwood, *Phys. Rev.*, (2), 1918, **12**, 448 (observations with Corning G-702-P glass). On the other hand, if an incandescent filament is present, the vacuum improves or "cleans up" with time, owing to ionization, sorption and reactions with the glass walls. See S. Dushman, *Production and Measurement of High Vacuum*, Chapter V (*General Electric Review*, Schenectady, N.Y., 1922). R. S. Willows (*Phil. Mag.*, (6), 1901, **1**, 503) in studying the sorption of gas in a Crookes tube found that with a volume of 108 c.c. and a pressure of 1 mm., a current of 10.8×10^{-4} amperes passing for thirty minutes reduced the pressure nearly one-eleventh. He found that most, if not all, of the gas sorbed was chemically combined with the glass, Jena glass sorbing less than lead-glass

requires much time (days) even at 500°. Jena glass tubing when heated above 600° C. yielded 3 c.c. or 5 mg. of gas per 10,000 sq. cm. of surface, the gas being mainly nitrogen together with oxygen and carbon dioxide.¹ These amounts are subject to large variation.²

Heating glass in air at atmospheric pressure always lessens the quantity of gas evolved upon subsequent vacuum heat treatment, even though the glass may be under normal atmospheric conditions for an interval of several months between the two processes.³ Menzies points out that heating glass to incipient fusion may seal capillaries in the surface.⁴

Rebbeck and Ferguson⁵ report very interesting and significant observations on electrolysis through glass at ordinary temperatures. It is well known that glass contains a framework of silica or silicate which acts as a large, immobile, negative radical through which positive ions, such as hydrogen ion or silver ion, migrate freely during electrolysis. Clean surfaces of alkali metals are made, even commercially, by electrolysis through glass walls. Glass membranes also function as hydrogen electrodes.

"When a tube of ordinary soda-lime glass is filled with mercury and subjected to electrolysis through the glass by applying a potential difference between the mercury and a suitable external conductor such as a liquid electrolyte, a

and this less than soda-glass; in the first two cases hydrogen is sorbed to a far less extent than air or nitrogen, which show little difference. See also the Research Staff of the General Electric Co. Limited, London, (*Phil. Mag.*, (6), 1920, **40**, 585; 1921, **41**, 685; 1921, **42**, 227; 1922, **43**, 914) who describe the balance between these phenomena and the effects of a coating of phosphorus, arsenic or sputtered metal, and develop a theory of adsorption of negative ions adhering (adsorbed) to a polar layer on the wall.

¹ M. Guichard, *Compt. rend.*, 1911, **152**, 876; *Bull. soc. chim.*, (4), 1911, **9**, 438. In each case he uses the expression, "a surface of 100 cm.", which we have here called 100 sq. cm.

² D. Ulrey, *Phys. Rev.*, (2), 1919, **14**, 160.

³ D. Ulrey, *Phys. Rev.*, (2), 1919, **14**, 160.

⁴ A. W. C. Menzies, *Nature*, 1930, **125**, 445.

⁵ J. W. Rebbeck and J. B. Ferguson, *J. Am. Chem. Soc.*, 1924, **46**, 1991.

coating of gas bubbles forms between the mercury and the glass when the mercury is cathode" ¹ but not when the mercury is anode. "Drying both the mercury and the glass previous to filling the tube with mercury does not prevent bubble formation, nor does filling the tubes by distillation in a good vacuum. When, however, the tubes are annealed, or baked out in a vacuum for many hours at high temperatures, little or no gas develops. Once the gas has formed it may be made to disappear by reversing the potential." ¹ Appreciable evolution of gas may be obtained through applying as little as 1.3 volts. The gas is mostly hydrogen, mixed with some oxygen. Evidence is given in favour of the view that the phenomena are due to the action of sodium upon water partly adsorbed and partly dissolved in the glass and the simultaneous electrolysis of the sodium hydroxide produced.

Swinton ² observed that the inner surface of vacuum tubes after cathode ray bombardment is roughened and, upon heating before the blowpipe, becomes clouded with minute bubbles of hydrogen, which he ascribes to electrolysis of the water on or in the walls of the vessel; the effect can be obtained by electrical induction without electrodes.

Manley ³ used an electric glow discharge to free the surface of glass from gases and vapours which could not be removed by mere evacuation. Pirani ⁴ used a glowing filament in a stream of mercury vapour for the same purpose. Risler, ⁵ on the other hand, compensates for the disappearance of gas

¹ J. W. Rebbeck and J. B. Ferguson, *J. Am. Chem. Soc.*, 1924, **46**, 1992.

² A. A. C. Swinton, *Proc. Roy. Soc. (London)*, A, 1907, **79**, 134; 1908, **81**, 453; *Chem. News*, 1907, **95**, 134. S. E. Hill (*Proc. Phys. Soc. London*, 1912, **25**, 35; *Electrician*, 1912, **70**, 184, 228) deduces chemical effects from the appearance of the vacuum tubes. See also M. Gouy, *Compt. rend.*, 1896, **122**, 775, and R. Pohl (*Verhandl. deut. physik. Ges.*, 1907, **9**, 306) who disagrees with Swinton; also W. D. Bancroft, *J. Phys. Chem.*, 1918, **22**, 345.

³ J. J. Manley, *Proc. Phys. Soc. London*, 1924, **36**, 288, 291.

⁴ M. Pirani, *Z. Physik*, 1922, **9**, 327.

⁵ J. Risler, *Compt. rend.*, 1927, **185**, 936.

in incandescent lamps and three electrode tubes, so-called "clean-up",¹ by including a small quantity of a compound like anthraquinone which gradually decomposes and sets free carbon dioxide. This is the opposite effect from that of the "getters," magnesium and calcium for oxygen, cæsium and sodium for hydrogen.

Willows and George² studied the sorption of gas by fused silica, brought about by electrical discharges. A new bulb of fused silica did not sorb air, but if fed with repeated doses of hydrogen—which are sorbed when an electrodeless discharge is passed—it then became very active. If discharges in hydrogen were alternated with those in air, the bulb could be made to sorb large quantities of either gas, and the activity with each gradually increased. The authors reject the theory of physical adsorption and also, in their own experiments at least, Swinton's theory that the gas is shot into the walls and held there. It is supposed that chemical actions occur with air, and oxidation products are formed; these are reduced by hydrogen.

Sorbed gases do not affect the electrical conductivity of glass even though the conductivity is noticeably decreased by heat treatment.³ Glass powder conducts well in an atmo-

¹ For general discussion, see S. Dushman, *Production and Measurement of High Vacuum*, Chapter V, page 165 (*General Electric Review*, Schenectady, N. Y., 1922), *J. Franklin Inst.*, 1931, **211**, 689. See also E. Pietsch, *Ergebnisse der exakten Naturwissenschaften*, 1926, **5**, 212. Langmuir's view is that clean-up or disappearance of practically all except the noble gases from a vacuum of a lighted tungsten lamp is purely chemical in nature. The four types of reaction are those in which: (1) the filament is attacked by the gas; (2) the gas reacts with the vapour given off by the filament; (3) the filament acts catalytically on the gas, producing a chemical change in the gas without any permanent change in the filament; (4) the gas is chemically changed, or is made to react with the filament by means of electrical discharges through the gas (I. Langmuir, *J. Am. Chem. Soc.*, 1912, **34**, 1310; 1913, **35**, 105, 931; 1915, **37**, 1157; 1916, **38**, 2279, 1919, **41**, 167; *Proc. Am. Inst. Elec. Eng.*, 1913, **32**, 1895; *Z. anorg. Chem.*, 1914, **85**, 261). For a discussion of "getters" (sorbing agents or reactive elements, usually phosphorus), see R. Andrews and J. S. Bacon, *J. Am. Chem. Soc.*, 1931, **53**, 1674.

² R. S. Willows and H. T. George, *Proc. Phys. Soc. London*, 1916, **28**, 124.

J. W. Rebbeck and J. B. Ferguson, *J. Am. Chem. Soc.*, 1924, **46**,

sphere of moderate relative humidity.¹ Kenrick and Giffen deduced from their observations an equilibrium between adsorbed water and water dissolved in the glass. Trouton² has pointed out that if the surface has been previously dried at a high temperature, the amount of moisture sorbed upon a surface from an atmosphere of less than 50 per cent relative humidity is small and does not greatly affect conductivity, but if the drying has been attempted at ordinary temperatures,³ condensation is greater and is accompanied by high conductivity. Shellac powder behaves similarly above and below a relative humidity of 90 per cent.

Sherwood⁴ and Harris and Schumacher⁵ are of the opinion that gases that are merely adsorbed are all removed when glass is heated to 200° C. or 300° C. because this corresponds approximately with the amounts that are resorbed on cooling. Anything evolved at higher temperatures is supposed to come from the interior of the glass. Manley,⁶ on the other hand, was of the opinion that the difficultly removable gas and vapour consisted of a primary skin upon the glass acquired during its first exposure to a gas and that ordinary sorption, forming a secondary skin, took place upon the primary skin. However, he noted that the amount of permanent gas of "primary" skin was enough to cover the glass 20 molecules deep. Langmuir⁷ deduces from the remarkable slowness with which moisture is given up on heating, the relatively large amounts involved, and the length of time required for its resorption, that most of it "penetrates to a very considerable depth into the surface".

2000; V. Bush and L. H. Connell, *J. Franklin Inst.*, 1922, **194**, 231.

¹ F. B. Kenrick and F. J. Giffen, *Coll. Sym. Mon.* (Toronto, 1928), 1928, **6**, 53. See also R. W. Bunsen, *Wied. Ann. der Physik*, 1885, **24**, 321, and many others.

² F. T. Trouton, *Report of the British Association for the Advancement of Science*, 1907, p. 453.

³ For the impossibility of drying glass at ordinary temperatures, see this chapter, pages 214, 222 and 224.

⁴ R. G. Sherwood, *Phys. Rev.*, (2), 1918, **12**, 448.

⁵ J. E. Harris and E. E. Schumacher, *Ind. Eng. Chem.*, 1923, **15**, 174.

⁶ J. J. Manley, *Proc. Phys. Soc. London*, 1924, **36**, 288 and 291.

⁷ I. Langmuir, *J. Am. Chem. Soc.*, 1916, **38**, 2284; 1918, **40**, 1387.

The presence of sorbed gases upon ordinary glass surfaces, and their partial removal by heating, is demonstrated by the experiments of Marcet.¹ Water boils in smooth glass vessels at about 101°C. , but if the vessel has been previously heated to 300° or 400°C. or even washed out with hot, concentrated sulphuric acid or alkali and rinsed, the superheating brings the boiling temperature to 104°C. with much bumping. The following observation of Jamin and Bertrand² may also be quoted.

“ A fine powder (pounded glass or oxide of zinc) is mixed in a mortar with water which has been deprived of air, so as to form a clear paste without any bubbles of gas ; this is poured into a flask with a long neck until it fills two-thirds of the bulb. After a short time the solid substance is deposited with a layer of water above it. A vacuum is then produced in the flask ; at the first strokes of the piston the water rises, increases in volume so as to fill the flask, but no bubble of air makes its appearance ; and if the cock of the air-pump be suddenly opened, the pressure is reproduced, and the fluid returns to its original volume with a rapidity which shakes the flask, and a sound like that of the water-hammer. If the experiment be prolonged, and the vacuum completely formed, noticeable quantities of bubbles are produced.”

GREASY FILMS UPON GLASS SURFACES

Waidele in 1843³ explained the “ breath figures ” of Moser as due to impurities other than water taken up by the glass. In this connexion it is of interest to mention the formation of “ film ” on polished glass surfaces⁴ in enclosures which are air and water tight.

“ By film is meant the coating of lens and prism surfaces with what is apparently a thin deposit of moisture. This has caused much trouble and annoyance, many instruments being rendered quite useless until taken apart and cleaned. The film appears

¹ F. Marcet, *Pogg. Ann. der Physik*, 1842, **57**, 218.

² J. Jamin and A. Bertrand, *Compt. rend.*, 1853, **36**, 994 ; *Phil. Mag.*, (4), 1853, **6**, 159.

³ E. Waidele, *Pogg. Ann. der Physik*, 1843, **59**, 255.

⁴ For a summary of the literature see G. W. Morey, *J. Optical Soc. Am.*, 1922, **6**, 688.

to have several characteristics. It apparently consists of a series of globules of moisture, forming patterns on the surface similar to those made by cleaning with a linen rag which has seen much service. Often a series of larger globules will occur, each surrounded by a clear space. Parts of a surface under pressure from mounts will be clear for a small space surrounding the points of contact, the clear space being fringed by a denser deposit. Prisms will often show a distinct pattern of the seat, the part covered by metal having a fairly dense deposit, a fairly clear space occurring where the surface is free, becoming again more dense away from the metal. A cut, scratch or hole in the surface is generally surrounded by a clear space, beyond which the deposit is more dense.

"If a drop of water from a pipette is allowed to run over a filmed surface, it will leave a track which is quite free from any trace of scum. Microscopic examination shows no injury to the surface after filming. Instruments such as telescopes, in which the air is occasionally changed, very seldom film. When they do, it is generally the case that they have been out of service for some time."¹

The cause of film has not yet been established. Two factors, however, seem to be necessary; namely, the presence of moisture and the presence of traces of grease. The grease may be derived from the breath, from aluminium or other porous metal which has been machined but not afterwards heated, from the neighbourhood of Japan or bitumen black, pitch or beeswax. Some compositions of glass are more susceptible than others.

SORPTION OF WATER

However water may be held by glass, whether partly in solution in the glass or in capillary pores in the surface products of decomposition, the retentivity of glass for the initial portion of the sorbed water is uncommonly high. Bunsen² passed a stream of highly desiccated air through glass wool for intervals of about twelve hours until no more water was given up to phosphorus pentoxide by the issuing gas. The experiment was continued at successively higher temperatures

¹ H. S. Ryland, *Trans. Optical Soc.* (London), 1918, **19**, 178.

² R. W. Bunsen, *Wied. Ann. der Physik*, 1885, **24**, 321.

and the amounts of water so obtained were compared with the apparent surface of the glass wool; that is, assuming it perfect and free from porosity or permeability. Assuming that all the water had been thus removed at 503°C. , the thickness of that which had been retained at previous lower temperatures was as follows, if the density of such water was unity throughout:

$^{\circ}\text{C.}$	468	415	329	215	107	23
$\text{\AA.}$	42	132	363	547	670	1,052

It is therefore not surprising that the extremely large amounts of water retained by the surface of glass carefully dried at moderate temperatures profoundly affect the extent to which other substances may be sorbed.

In studying the sorption of water by glass, the most obvious source of disturbance is the solubility of the glass or the alkali thereof. This may cause deposition of large amounts of water, owing to the lowering of vapour pressure so produced, as was pointed out by Faraday.¹ Similarly, Warburg and Ihmori² found no measurable film of water deposited upon glass surfaces coated with silica or free from alkali at relative humidities up to 95 per cent. Only freshly blown, fire polished or otherwise alkaline glasses took up sufficiently large amounts of water to be measured by their microbalance, which was sensitive only to a film 10–20 $\text{\AA.}$ deep. Previous washing for five minutes with boiling water rendered the deposition of moisture almost or quite too small for measurement.³ Harris and Schumacher⁴ found a definite relation between

¹ M. Faraday, *Phil. Trans. Roy. Soc. London*, 1830, Part I, page 49.

² E. Warburg and T. Ihmori, *Wied. Ann. der Physik*, 1886, **27**, 481. J. Giesen (*Ann. der Physik*, (4), 1903, **10**, 830) likewise found no sorption of water if a glass were previously washed with boiling distilled water; otherwise the amount of water corresponded to a depth of 300 to 350 $\text{\AA.}$ With aluminium, an alloy of zinc and copper, and an alloy of zinc and tin the thicknesses were about 4 $\text{\AA.}$, 1 $\text{\AA.}$ and 1 $\text{\AA.}$, respectively.

³ T. Ihmori (*Wied. Ann. der Physik*, 1887, **31**, 1014) found higher results with Jena glass even after washing, as for example, 35 to 64 $\text{\AA.}$ at a relative humidity of 88 per cent.

⁴ J. E. Harris and E. E. Schumacher, *Ind. Eng. Chem.*, 1923, **15**, 175.

the amount of water vapour held by a glass and its alkali content.

It is certain, however, that sufficient water vapour can be sorbed at high relative humidities to affect the results of quantitative analysis,¹ spectrum analysis,² measurements of vapour pressure by the dynamic method,³ determinations of vapour density, specific heat,⁴ conduction of heat,⁵ etc. Parks⁴ found that glass wool, and precipitated silica, when exposed to fully saturated water vapour in the presence of air had taken up an amount equal to a layer 1,330 Å. deep; with saturated vapour such results may be fortuitous, as the conditions are not sufficiently defined. However, Parks shows that various experiments by investigators in other fields may be interpreted as being due to films of the same order of magnitude as those found by himself. Parks⁶ incidentally deduced that the specific heat of water on powdered silica was sensibly equal to unity, but this is subject to serious error because in the experiment 200 g. of water were used with 4 g. of powder.

Glass wool was studied by Trouton.⁷ It was dried in vacuo at 160°C. by exposure to phosphorus pentoxide for about seventy hours. Thereupon sorption appeared to proceed with difficulty and to pass through a stage of super-saturation, the isotherms exhibiting a maximum and minimum. With less thoroughly dried glass the effect was minimized or eliminated, as if nuclei were now present upon which sorption could proceed freely. These findings have not been further investigated. Strömberg,⁸ however, obtained a

¹ F. T. Allen and E. G. Zies, *J. Am. Ceram. Soc.*, 1918, **1**, 739.

² J. Trowbridge, *Phil. Mag.*, (6), 1902, **4**, 156.

³ A. W. C. Menzies, *J. Am. Chem. Soc.*, 1920, **42**, 985.

⁴ G. J. Parks, *Phil. Mag.*, (6), 1903, **5**, 517.

⁵ A. Kundt and E. Warburg, *Pogg. Ann. der Physik*, 1875, **156**, 182.

⁶ G. J. Parks, *Phil. Mag.*, (6), 1902, **4**, 252.

⁷ F. T. Trouton, *Proc. Roy. Soc. (London)*, A, 1907, **79**, 383; see also O. Masson (*Proc. Roy. Soc. (London)*, A, 1904, **74**, 230) who used a thermometer to detect sorption by the heat evolved.

⁸ R. Strömberg, *Kgl. Svenska Vetenskapsakad. Handl.*, (3), 1928, **6**, No. 2, 76.

point at $p/p_s = 48.6$ per cent which lay above the smooth curve for glass.

SORPTION OF WATER ON GLASS SURFACES OF SUPPOSEDLY KNOWN AREA

The true extent of the surface of glass in its ordinary condition is not even approximately known; the uncertainty amounts to an order of magnitude.

d'Huart ¹ found that when known quantities of water were introduced into an evacuated glass vessel and the resulting pressures were measured by means of a mercury manometer and compared with those predicted from the gas laws, the amount sorbed was proportional to the pressure and to the area of the glass. In accordance with the measurements of Bunsen in 1885 (this chapter, page 221), even at a vapour pressure as low as that obtained by evacuation in the presence of phosphorus pentoxide, there remained sorbed about 0.009 mg. of water per square centimetre. Alcohol, chloroform, benzene and toluene were much less sorbed than water vapour.

Langmuir ² heated microscope cover glasses (previously bent in a gas flame) in vacuo to 300° C. and found the following amounts of material given off per 10,000 sq. cm.: water, 1.8 c.c. = 4.5 molecules deep; ³ carbon dioxide, 0.3 c.c. = 1.05 molecules deep; and nitrogen, 0.25 c.c. = 0.9 molecules deep. Previous experiments with lamp bulbs ⁴ had given an evolution of water vapour of 10 c.c. at 200° C., 15 c.c. at 350° and 22 c.c. at 450° per 10,000 sq. cm. of apparent surface of glass.

A method was devised by McHaffie and Lenher ⁵ for study-

¹ d'Huart, *Compt. rend.*, 1925, **180**, 1594.

² I. Langmuir, *J. Am. Chem. Soc.*, 1918, **40**, 1387.

³ J. W. Rebbeck and J. B. Ferguson (*J. Am. Chem. Soc.*, 1924, **46**, 1999) by their electrolytic method arrived at a similar result for the amount of adsorbed water.

⁴ I. Langmuir, *Trans. Am. Inst. Elec. Eng.*, 1913, **32**, 1921; *J. Am. Chem. Soc.*, 1916, **38**, 2283.

⁵ I. R. McHaffie and S. Lenher, *J. Chem. Soc.*, 1925, **127**, 1559; S. Lenher and I. R. McHaffie, *J. Phys. Chem.*, 1927, **31**, 719; S. Lenher, *J. Chem. Soc.*, **1926**, 1785.

ing sorption or condensation at high relative humidities. An evacuated bulb (*A*) of known volume and internal area was filled with unsaturated water vapour at an elevated temperature such as 50° C. and the pressure measured at successively lower temperatures. At first the decrease in pressure was a linear function of the absolute temperature in agreement with the behaviour of a perfect gas. Hence, by neglecting sorption or considering it constant, the amount of water vapour could be calculated. At some lower temperature the experimental pressure begins to fall below the linear extension of the pressure-temperature curve as water is removed by sorption. The measurements can be continued at successively lower temperatures until the observed pressure becomes equal to the vapour pressure of water at that temperature. The observations were reproducible when approached from either side. The apparatus employed is shown in fig. 78¹ and typical curves are given in fig. 79² where *ao* is the established vapour pressure curve of liquid water.

It will be noted that the curves do not quite coincide with the true vapour pressure curve *ao* but fall distinctly below it. This is in accordance with the experience of Frazer, Patrick and Smith³ who found it to be due to alkali from the glass dissolving in the water and lowering its vapour pressure.

The amounts of sorption deduced from the points on the curves in fig. 79 are shown in fig. 80. The ordinates are numbers of complete layers of molecules, assuming that each molecule covers a square of apparent surface equal to 8.4×10^{-16} sq. cm. The values vary from 0 to 184 for glass, from 0 to 48.6 for fused silica,⁴ and from 0 to 38.9 for platinum

¹ I. R. McHaffie and S. Lenher, *J. Chem. Soc.*, 1925, **127**, 1561, fig. 1.

² I. R. McHaffie and S. Lenher, *J. Chem. Soc.*, 1925, **127**, 1565, fig. 2.

³ J. C. W. Frazer, W. A. Patrick and H. E. Smith, *J. Phys. Chem.*, 1927, **31**, 897.

⁴ Cleaned with organic solvents, hot freshly prepared chromic acid, and concentrated nitric acid; repeatedly washed with distilled water and dried. The extent to which such a surface has been acted upon is unknown; on the other hand, fused silica is exceptionally subject

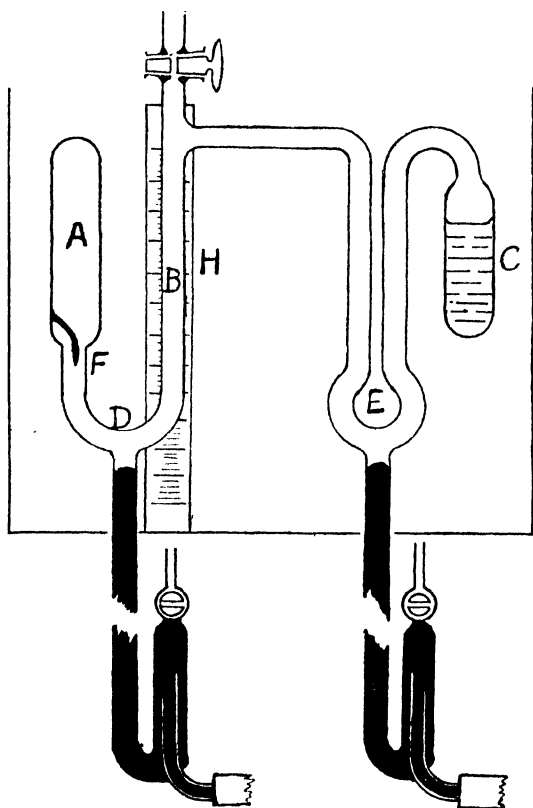


Fig. 78.—Apparatus of Lenher and McHaffie for studying the Sorption of Water Vapour by Glass.

polished with rouge and chamois and thoroughly cleaned with concentrated nitric acid. These would correspond with layers

to attack by alkali. For example, the author has observed that a dilute solution of alkali may set to a jelly upon cooling after it has been heated for a short time at 90° in a test tube made of fused silica. A. A. Griffith (*Phil. Trans. Roy. Soc. London*, 1920, **221**, 163) has shown that freshly drawn fibres of fused silica are almost immediately so attacked by ordinary air that their apparent tensile strength is enormously diminished.

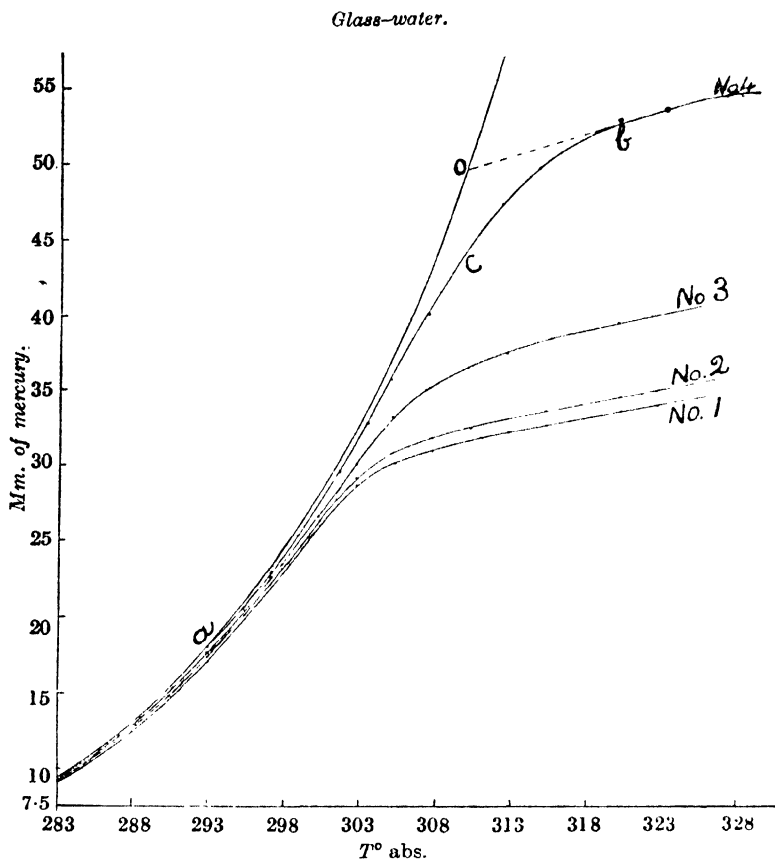


Fig. 79.—Pressure observed with a known amount of Vapour in a Bulb of Constant Volume as the Temperature is lowered from the region in which the Linear Gas Law obtains to that where the Pressure observed coincides with the Vapour Pressure of Liquid Water (McHaffie and Lenher).

up to 530 Å. thick for glass, 136 Å. for fused silica, and 113 Å. for platinum if the surfaces were plane and uncorroded.

Lenher,¹ struck by the fact that his curves of the amount of sorption *reach* the pressure axis at comparatively high

¹ S. Lenher, *J. Chem. Soc.*, **1926**, 1785.

pressures, thus indicating no sorption at or below such pressures, makes a suggestion which appears to be in error because it aggravates the difficulty. He assumes that the curves as drawn represent only the building up of the multi-molecular

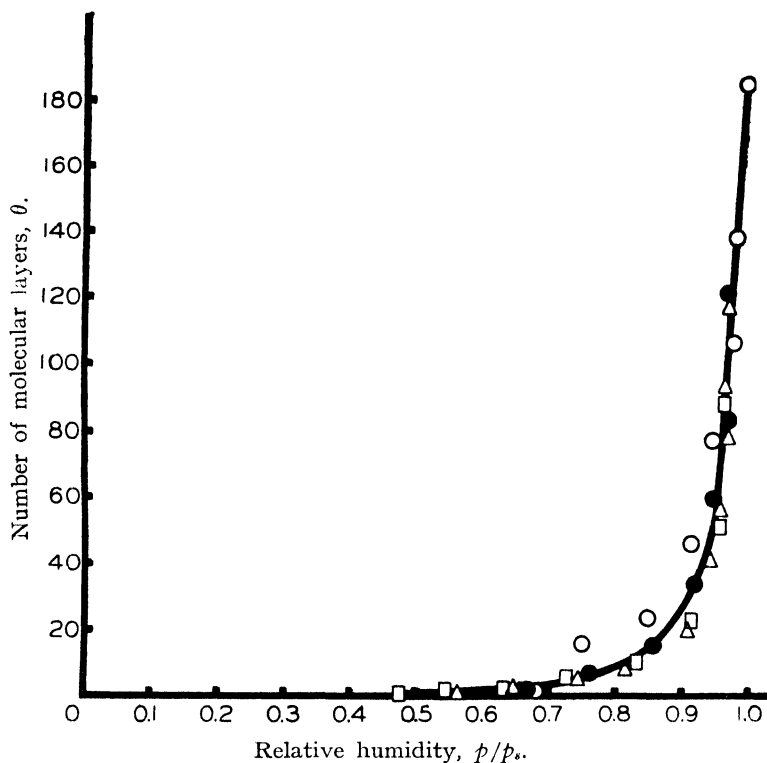


Fig. 80.—Sorption of Water Vapour by Glass at 20°–50° C., according to McHaffie and Lenher. One Molecular Layer equals 3.5×10^{-6} Grams of Water per sq. cm. □—No. 1; △—No. 2; ●—No. 3; ○—No. 4.

film at high pressures and that *between* them and the pressure axis there is a line, *at right angles to the pressure axis*, connecting with a sorption isotherm, still closer to the pressure axis, the isotherm finally leading to the point of zero pressure and zero sorption.

Frank¹ has carried out a precise determination of the initial part of the sorption isotherm on a surface of Pyrex glass which had been treated for a week with chromic acid cleaning solution which was several times heated to boiling. The initial portion of the isotherm obtained at 20° is repro-

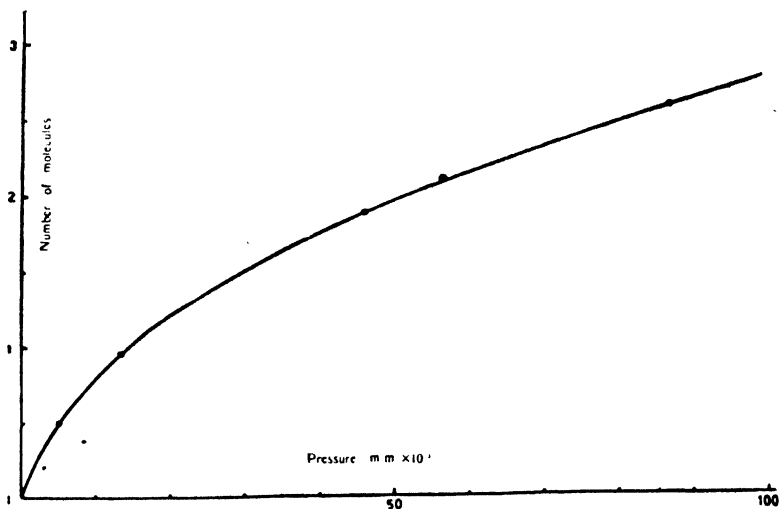


Fig. 81.—Frank's Sorption Isotherms for Water on a Washed Glass Surface at Pressures up to 0.1 mm.

duced in fig. 81² in which the ordinates are numbers of molecular layers per square centimetre (apparent), assuming that each molecule of water covers 16 sq. Å. of the hypothetical plane surface. The three square points towards the origin are due to traces of foreign gas in the glass of the small capsules in which the water vapour was introduced when the precaution had not been taken of first baking them out in vacuo. The values approached constancy within ten or fifteen minutes.

¹ H. S. Frank, *J. Phys. Chem.*, 1929, **33**, 970. Compare E. K. Carver, *J. Am. Chem. Soc.*, 1923, **45**, 63 (this chapter, page 234).

² H. S. Frank, *J. Phys. Chem.*, 1929, **33**, 975, fig. 6.

Strömberg¹ suspended thin plates of Jena glass and fused silica from a microbalance over various solutions of sulphuric acid of known relative humidity. The glass, like the fused silica, was previously boiled for hours in aqua regia, then in concentrated nitric acid and finally in several changes of distilled water. After drying for two hours at 200°C., the glass was then evacuated at 145°C. At 18.1°C. with a vapour pressure of 3.83 mm. the amount of water vapour sorbed compared with the apparent surface was equivalent to a layer 72 Å. or 28.2 molecular diameters thick and with saturated vapour, 15.58 mm., 737 Å. or 283 molecular diameters. Values obtained by desorption were far greater than those attained by direct sorption. This hysteresis was peculiar to the glass, and was considered to show that something besides pure adsorption was taking place. For the fused silica the maximum apparent thickness, with saturated vapour, was 135 Å.

The only such experiments upon glass surfaces not previously exposed to water or other liquids are those of Frazer, Patrick and Smith.² They used the method of McHaffie and Lenher and obtained no indication of sorption either of toluene or of water upon such a fresh glass surface; the method, of course, would not detect a constant or monomolecular layer. They obtained condensation with toluene and with water similar to the results of McHaffie and Lenher when they used surfaces that had been washed. Their comments are "but it is surely absurd to attempt to calculate the thickness of this adsorbed layer, for we have absolutely no information regarding the extent of the surface" and "we do not know how much the vapour pressure is reduced by the solutes present, or by the capillary action of the amorphous silica". They point out that the presence of 0.2 mg. of silica gel would account for the maximum sorption of toluene observed.

¹ R. Strömberg, *Kgl. Svenska Vetenskapsakad. Handl.*, (3), 1928, **6**, No. 2, 1.

² J. C. W. Frazer, W. A. Patrick and H. E. Smith, *J. Phys. Chem.*, 1927, **31**, 897.

Fig. 82¹ is of particular interest because curve 4 referred to a glass surface which had never come into contact with liquid water and in which the observations were made at successively lower temperatures. Curves 5 and 6, in which the rounding off and lowering indicates condensation, were obtained by successive reheatings of the bulb with the condensed water remaining over from curve 4. When such a

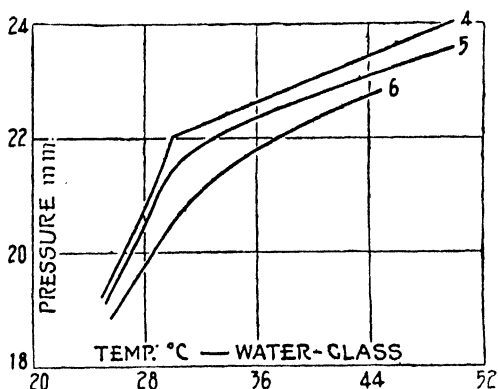


Fig. 82.—Sorption of Water Vapour by Glass (Frazer, Patrick and Smith).

glass bulb was allowed to stand for four months, only a vapour pressure curve was obtained, indicating that the action upon the glass had proceeded until a saturated solution was present on the surface.

An optical method based upon the ellipticity of light reflected from a surface at the polarizing angle has been used by Frazer.² The method was probably capable of detecting

¹ J. C. W. Frazer, W. A. Patrick and H. E. Smith, *J. Phys. Chem.*, 1927, **31**, 904, fig. 4. K. Herzfeld and J. H. Frazer (*Phys. Rev.*, (2), 1928, **31**, 1110), using an improved method sensitive to 1 Å., found no adsorption of water on glass up to 1 mm. pressure and a layer less than one molecule thick up to the saturation point, 21 mm.

² J. H. Frazer, *Phys. Rev.*, (2), 1929, **33**, 97. Further measurements were made with Pyrex glass by A. S. Adams (*Phys. Rev.*, (2), 1929, **34**, 1438) showing changes with time and an irregular decrease with rise of temperature to 290°C. (See also Chapter II, page 26.)

a change in thickness of sorbed layer of 3 Å. It was applied to freshly broken surfaces of plate glass (possibly already covered with a monomolecular layer of water vapour derived from local heating of the glass and held by chemo-sorption). His results for water vapour and methyl alcohol vapour at room temperature (pressure of saturated water vapour, $p_s = 18$ mm.) are shown in fig. 83.¹ The rapid growth at higher relative pressures is ascribed to dissolving alkali with consequent lowering of vapour pressure, although the observa-

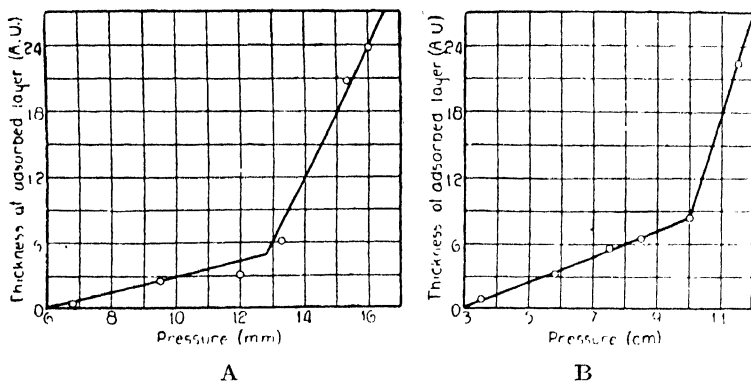


Fig. 83.—A—Sorption of Water Vapour on Glass.
B—Sorption of Methyl Alcohol Vapour on Glass.

tions were reversible except when 1 per cent of hydrochloric acid gas was admitted with the vapour. Wholly negative results were obtained in experiments with nitromethane, acetone, toluene, and formaldehyde; all of which did not condense on the glass even at saturation pressures.

Pettijohn² attempted an unusual method of determining

¹ J. H. Frazer, *Phys. Rev.*, (2), 1929, **33**, 103, figs. 1 and 2.

² E. Pettijohn, *J. Am. Chem. Soc.*, 1919, **41**, 477. However, the clinging of particles to each other and to walls under water is due to a different mechanism than in gases; it takes place through thick polarized layers of solvent or solvate water; see for example, A. von Buzágh, *Kolloid-Z.*, 1930, **51**, 105, 230; 1930, **52**, 46.

the amount of sorbed water on a supposedly known surface. He measured the minimum amount of water which it was necessary to add, drop by drop, until most of the glass pearls or particles of sand stuck to the glass walls of the vessel. With eight very different liquids such as water, toluol and pyridine the amount of liquid required was independent of the kind of liquid, and the film thickness of the adhesive layer calculated for the apparent surface of sand and pearls was of the order of 1,000 Å. Tammann¹ noticed that a hot powder such as charcoal sticks to a cold glass wall. This was attributed by Valentiner² to the heated powder sorbing some of the gas previously adsorbed on the cold glass surface. It appears to the writer more probable that when the powder momentarily denudes the surface, the material which it has sorbed does not fully cover its porous surface; hence, bare glass surface comes into direct contact with bare points on the powder and a direct union results in the powder being held.

Drucker and Marxen³ found that glass wool at 25° sorbed fourteen times as much carbon dioxide after it had been exposed to water vapour at 5.4 mm. pressure; even sorption of hydrogen became appreciable thereby. Compared as usual with the apparent surface of the glass wool, the thickness of the water layer appeared as 5.5 Å., that of the hydrogen 1 Å., and that of the carbon dioxide up to 20 Å. (assuming its density as 0.7), whereas without the water it had been only 1.0 Å. deep.

¹ G. Tammann, *Ann. der Physik*, (4), 1905, **18**, 856; W. Biltz, *Ann. der Physik*, (4), 1910, **31**, 1050.

² S. Valentiner, *Elster-Grütel-Festschrift*, 1915, p. 284.

³ C. Drucker, *Z. Elektrochem.*, 1929, **35**, 641; C. Drucker and J. Marxen, *Z. physik. Chem.*, Abt. A, 1930, **147**, 371. In these papers and an earlier one (C. Drucker, *Z. physik. Chem.*, 1918, **92**, 289; see also W. Gaede, *Ann. der Physik*, (4), 1913, **411**, 289) Drucker points out the parallelism between the sorptive behaviour of various gases and their mixtures, in particular with charcoal and glass, and the curves for viscosity as measured in glass tubes, and he surmises that this is to be ascribed to the formation of sorbed layers differing in concentration and composition from the main stream of gas.

SORPTION OF OTHER SUBSTANCES ON GLASS SURFACES OF
SUPPOSEDLY KNOWN AREA

Frazer, Patrick and Smith¹ have extended their work on "virgin" glass surfaces to measurements with toluene, using the method of McHaffie and Lenher, and found no indication of any sorption until after the glass surface had been washed and therefore leached out or corroded. It will be remembered that this method does not detect a constant amount of adsorption uninfluenced by pressure changes in the higher ranges of relative humidity and is not sensitive enough to detect a monomolecular layer. Latham² repeated their work with the same finding and obtained similar results with acetonitrile, nitromethane, and with bulbs in which a minute fragment of silica gel had been placed.

Recently, however, Curry³ has extended this method by measuring the amount of gas desorbed upon heating the glass after the experiment. A glass capillary was used in order to have a large surface in comparison with the volume, and the walls were smoothed by maintaining the tube at a temperature near the softening point for some time. In experiments on sorption at 25°C. and -78°C. and subsequent desorption, using ethylene, carbon monoxide, toluene, ammonia, hydrogen, air and carbon dioxide, the amount desorbed approached that for a monomolecular layer for -78°C. and a fraction thereof for 25°C. Preliminary exposure to the vapour of water increased the amounts of toluene and hydrogen sorbed and desorbed by about three-fold and a similar result was obtained with the water vapour itself.

An exact determination of the sorption of toluene by Pyrex glass, which had been washed for hours with hot chromic acid cleaning solution and steamed out, was made by Carver.⁴ When the glass was evacuated at 100°C., the sorption was slight and uncertain. When the evacuation was

¹ J. C. W. Frazer, W. A. Patrick and H. E. Smith, *J. Phys. Chem.*, 1927, **31**, 897.

² G. H. Latham, *J. Am. Chem. Soc.*, 1928, **50**, 2987.

³ J. R. Curry, *J. Phys. Chem.*, 1931, **35**, 859.

⁴ E. K. Carver, *J. Am. Chem. Soc.*, 1923, **45**, 63.

carried out at 200° C. for six hours, the sorption of toluene was much below that observed when the evacuation was continued for twelve hours; and only in the latter case did the sorption isotherm approach the form of the Langmuir equation. Even so at a pressure of 0.26 mm. at 0° C. the amount sorbed would not have been sufficient to cover more than 28 per cent of the apparent surface (not allowing for corrosion) with a single layer of molecules. Under the same conditions, the sorption of hydrogen could not be detected.

Paranjpe,¹ using fused silica, at —190° C. found that hydrogen was sorbed to the extent of 0.2 c.c. at 25 mm. and 1.05 c.c. at 350 mm. per 10,000 sq. cm. of surface (corrected to N.T.P.).

Langmuir² showed that atomic hydrogen, produced by heating a metallic wire in dry hydrogen at very low pressures, is sorbed with remarkable intensity. The sorbed film can remain unchanged on glass at liquid air temperature for several days. The amount never exceeded that corresponding to a monatomic layer on the apparent surface. Fresh atoms of hydrogen striking any already on the surface combine with and remove them. Similar experiments with atomic iodine and glass have been made by Bonhoeffer.³

With the same surfaces of glass, fused silica and platinum which had been used for water Lenher⁴ obtained results with benzene similar to those with water. Maximum thicknesses at saturated humidity, $p = p_s$, for benzene were as follows: on glass 110 Å.; on platinum 700, 930 and 550 Å. at 22.4°, 26.9° and 31° C., respectively; on silica 190 Å. at 19° and 120 Å. at 28.7° C.

Smits and Purcell,⁵ using Lenher's method, found that glass sorbed 300 molecular layers of ammonium bromide at 379° C.

¹ G. R. Paranjpe, *Proc. Asiatic Soc. Bengal*, 1919, **15**, 136.

² I. Langmuir, *J. Am. Chem. Soc.*, 1912, **34**, 1310; 1916, **38**, 2270.

³ K. F. Bonhoeffer and L. Farkas, *Z. physik. Chem.*, 1928, **132**, 235.

⁴ S. Lenher, *J. Chem. Soc.*, **1927**, 272.

⁵ A. Smits, *J. Chem. Soc.*, **1928**, 2953; A. Smits and R. Purcell, *J. Chem. Soc.*, **1928**, 2942. Smits adds the information that Jena glass and fused silica which had not been allowed to come into contact with water or water vapour were also employed.

Rinse¹ by the same method found that glass at 300° C. could take up as much as 667 molecular layers of mercuric iodide, even with "virgin" "fire polished" surfaces,² such as were used by Frazer, Patrick and Smith. No reaction could be detected between the glass and mercuric iodide. The effect was independent of the degree of dryness. Similar results were obtained with ordinary glass, using mercuric chloride, mercuric bromide and iodine, but not with mercurous chloride and mercury.

Benzophenone is sorbed by glass tubes through the saturated vapour phase to the extent of only 0.076 mg. per 10,000 sq. cm. of apparent surface as measured by Volmer and Adhikari.³ This amounts to only a few per cent of a monomolecular layer.

Unmindful of the uncertainty as to the extent and nature of the surface of glass, Evans and George⁴ attempted to standardize the earlier work of Mülfarth⁵ by themselves measuring the amount of dry carbon dioxide which was sorbed by ordinary (soft) glass wool previously evacuated at 300° C. Assuming a density in the sorbed layer equal to that of liquid carbon dioxide and that a monomolecular layer would be 5.1 Å. thick, they deduced from their results that at 0° and one atmosphere there were 5.5 layers of carbon dioxide upon the apparent surface of the glass wool; ⁶ that is, 1 c.c. at N.T.P. to 10,000 sq. cm. Similarly, they deduced 23 layers of ammonia. From the results for carbon dioxide they recalculated Mülfarth's data as representing 32 layers of sulphur dioxide,⁷ 40 layers of ammonia, 4.5 of nitrous oxide and 3.5 of acetylene. Reference to this chapter, page 239,

¹ J. Rinse, *J. Chem. Soc.*, **1928**, 1442.

² But see Chapter X, page 327.

³ M. Volmer and G. Adhikari, *Z. physik. Chem.*, 1926, **119**, 46.

⁴ M. H. Evans and H. J. George, *Proc. Roy. Soc. (London)*, A, 1923, **103**, 190.

⁵ P. Mülfarth, *Ann. der Physik* (4), 1900, **3**, 328.

⁶ Similarly, D. H. Bangham and W. Sever (*Phil. Mag.*, (6), 1925, **49**, 942.

⁷ Similarly, D. O. Shiels (*J. Phys. Chem.*, 1929, **33**, 1178) found about ten layers at 5.7 cm. pressure at 25° C.

will show that these calculations are fallacious on account of the difference in the kind of glass used by Mülfarth as well as the thorough preliminary drying which he employed.

These results may be compared with the isotherms of Miss Isselstein ¹ for carbon disulphide, pentane and methyl chloride which gave layers apparently as much as 35 molecules deep. She used powdered glass that had been extracted with hydrochloric acid and dried at 160° after many washings. The surface was estimated by determining the amount of ethyl violet and diamond fuchsine which was sorbed. The powder was covered with the liquid which was then removed in successive portions by evacuation. Only the upper portions of the isotherms were studied, and she considered that capillary condensation in bulk could be neglected. However, it would require an S-shaped curve to connect her isotherms with the origin. Her results therefore lie open to interpretation as sorption plus capillary condensation like those elucidated by Bray and Draper (Chapter VI, page 210, and Chapter XVI, pages 441 and 442; also Chapter X, page 339).

Wulff ² states that "iodine deposits resulting from directional molecular rays, as in the Dunoyer experiments (C. R. **152**, 592-594; 1911), showed that those of a homogeneous nature are only possible on smooth, clean, perfectly annealed surfaces. On a surface, which was etched, rubbed or scratched in any particular portion, crystal nuclei started growing immediately" and

"adsorption experiments on glass surfaces of known curvature carried out on a long series of glass tubing, and on plane glass of different varieties, show similar functional relations to the results for deposition and reaction. Such thin layers can be weighed with a micro-balance. For plane and slightly curved surfaces the sorption layer does not exceed monomolecular thickness . . . but with increasing curvature the adsorbed layer increases. In capillaries 0.8 mm. in diameter and less, the adsorbed layer is of the order of 7 molecules in thickness."

¹ M. T. Isselstein, *Physik. Z.*, 1928, **29**, 873.

² J. Wulff, *Nature*, 1929, **123**, 682. See also Chapter IX, page 307, and Chapter XVIII, page 485.

SORPTION OF CARBON DIOXIDE AND OTHER SOLUBLE
CORROSIVE GASES

The most careful and extensive of the older work is that of Bunsen.¹ He studied the sorption of carbon dioxide by glass wool that contained the ordinary large amounts of water remaining on the surface of glass which is dried at ordinary temperature; that is, about 0.001 mg. per sq. cm. and several times this for glass which had not been washed.² He found that 136,280 sq. cm. took up in the first year 42.9 c.c., in the second year 15.03 c.c., and in the third year 12.04 c.c. of carbon dioxide; that is, a total of 5.135 c.c. of carbon dioxide at N.T.P. on 10,000 sq. cm. of apparent surface. This Bunsen himself afterwards ascribed to chemical attack by carbonic acid.³ Bunsen found that carbon dioxide was similarly taken up from the atmosphere. Krause⁴ repeated and confirmed these observations, using both fresh glass wool and some which had been partially extracted by boiling water; in the second case the amounts taken up were much less.

Both Bunsen and Krause found that if the fibres were previously dried at 500°C., the amounts of carbon dioxide sorbed remained below their limit of measurement even after a longer period. If water vapour was admitted, carbon dioxide immediately began to be taken up, especially by the more alkaline surface, to the extent of several hundred or thousand volumes of carbon dioxide for each volume of liquid water admitted; that is, four parts by weight of carbon dioxide to one of water.

Finally, Bunsen extracted the glass wool which had been used in his experiments with pure cold water, evaporated this to dryness, found that it effervesced with hydrochloric acid and, after determining sodium and silica, deduced that

¹ R. W. Bunsen, *Wied. Ann. der Physik*, 1883, **20**, 545; 1884, **22**, 145; 1885, **24**, 321; 1886, **29**, 161.

² See H. Krause, *Wied. Ann. der Physik*, 1889, **36**, 935.

³ See also the further arguments advanced by Wilhelm Ostwald (*Lehrbuch der allgem. Chemie*, 2 Aufl., Bd. II, Abt. 3, p. 244 (1906)) in his partial summary of the older literature.

⁴ H. Krause, *Wied. Ann. der Physik*, 1889, **36**, 923.

5.83 per cent by weight of the glass wool had been decomposed. He concluded that glass is a thoroughly useless material for the study of sorption.

These results were questioned by Mülfarth,¹ who used a powder of hard glass washed with water to which after careful drying not $\frac{1}{50}$ as much water had been restored as was present in Bunsen's experiments. Mülfarth did observe small but measurable amounts of sorption of carbon dioxide, sulphur dioxide, nitrous oxide, ammonia and acetylene on glass powder evacuated at 400° C. (see this chapter, page 236). The sorption was completed in two hours. When the glass had been evacuated at 500° C., the sorption was still measurable, being 2.05 c.c. (N.T.P.) at 22° C. and 604.8 mm. pressure by about 107 c.c. of powder. The amount sorbed increased somewhat less than in proportion to the pressure. The sorption is slightly greater at 0°. The results for the other gases are similar and in the order previously indicated (this chapter, page 236). However, the author's statement that Henry's law was obeyed is erroneous, especially for sulphur dioxide and ammonia, because the portions of the isotherms studied do not point towards the origin but rather towards a moderate amount of sorption at zero pressure.

The sorption of water vapour, carbon dioxide and hydrogen was studied by Mehlhorn,² using 3,600 sq. cm. of pieces of thin bulbs of soft glass evacuated at room temperature. The gas given off at 430° C. and not immediately taken up again on cooling amounted to 0.7 c.c., consisting of 83 per cent of carbon dioxide, neglecting water. In six successive experiments, after exposing to water vapour and admitting air which was free from carbon dioxide, the gas evolved was about 0.01 c.c. and consisted of about 70 per cent carbon dioxide. In seven further experiments with hydrogen the amounts evolved fell to 0.004 c.c. each time and consisted of 60 per cent of carbon dioxide. The total amount of carbon dioxide was smaller than that observed in Bunsen's experi-

¹ P. Mülfarth, *Drude Ann. der Physik*, (4), 1900, 3, 328.

² F. Mehlhorn (and E. Warburg), *Verhandl. physik. Ges. Berlin*, 1898, 17, 123.

ments, but so, in all probability, was the amount of water present. The experiments illustrate the extreme difficulty or impossibility of removing the whole of the carbon dioxide from glass, presumably due to its origin in the interior of the glass. Further measurements of the amount of water vapour, carbon dioxide and permanent gas evolved on heating glass (cleaned with chromic acid, washed and evacuated) at 400° C. have been published by Harris and Schumacher ¹ who show that the water and carbon dioxide are parallel to the alkali content of the glass, whilst the permanent gases are independent thereof. The latter usually amount to 0.4 c.c. on 10,000 sq. cm., whereas the carbon dioxide and water ranged from similar low values up to 10 or 100 times as much, respectively.

Magnus ² demonstrated that the sorption of sulphur dioxide by glass is sufficient to affect measurements of its volume or coefficient of expansion. He found that at least 0.8 c.c. more was sorbed per 10,000 sq. cm. of apparent surface at 0° than at 100°. However, Chappuis ³ found that the amounts liberated by 10,000 sq. cm. of apparent surface upon heating from 0° to 180° C. were 1.5 c.c. of sulphur dioxide, 1.02 c.c. of carbon dioxide, 2.21 c.c. of ammonia, 0.70 c.c. of hydrogen and 0.90 c.c. of air. Had this been the true surface of the glass, the hydrogen and oxygen would have been $\frac{1}{4}$ and $\frac{1}{2}$ enough for a monomolecular layer and the sulphur dioxide and ammonia enough for a double molecular layer. Hence the true values are much less.

Kayser ⁴ demonstrated with spun glass fibres as well as powdered glass that the surface area was not the sole factor determining the amount of sorption with different specimens even of the same glass. Durau has recalculated some of

¹ J. E. Harris and E. E. Schumacher, *Ind. Eng. Chem.*, 1923, **15**, 175.

² G. Magnus, *Pogg. Ann. der Physik*, 1853, **89**, 604.

³ P. Chappuis, *Wied. Ann. der Physik*, 1879, **8**, 24. Chappuis misquoted Magnus' number and in calculating his own from the values for one square metre to one square centimetre multiplied by 1,000 instead of 10,000.

⁴ H. Kayser, *Wied. Ann. der Physik*, 1881, **14**, 450.

Kayser's isotherms at 0° C. for ammonia and sulphur dioxide which exhibit amounts of sorption between a fraction of that required to cover the apparent surface with a monomolecular layer and values sufficient for several such layers. His glass was evacuated at 300° C.

Incidental to their experiments upon the time relations of sorption, Bangham and Burt¹ observed that the classical sorption isotherm held for sorption by glass wool (evacuated at 200° C.) if the value of n was taken equal to 4.2 for carbon dioxide, 3.2 for nitrous oxide, 10.7 for sulphur dioxide,² 3.7 for acetylene and 6 for ammonia. The amounts were roughly parallel with the solubility in water and the value of n , and, when related to the apparent surface, of course greatly exceeded the amounts required for a monomolecular layer. Ammonia was sorbed about five times more than carbon dioxide. With sulphur dioxide, evacuation at 200° C. is entirely inadequate for its removal from glass.

The careful work of Durau³ is deserving of special mention on account of the thorough standardization of the experimental materials and the conditions of experiment. The specimen of glass was selected after careful investigation of its suitability for trustworthy measurement of the extent of its surface by the methods of Wolff, Schmidt and Durau, and Schelte which are described in Chapter X. The powdered glass was evacuated for many days at 570° C. However, glass powder thoroughly evacuated at 600° C. gave off further gas at 740° C. and still more at 1,060° C., in each case reaching an equilibrium value. Only a portion could be resorbed on cooling and it became evident that these gases were coming from the interior of the glass, whether solid or melted. 120 g. of the evacuated

¹ D. H. Bangham and F. P. Burt, *Proc. Roy. Soc. (London)*, A, 1924, **105**, 481; *J. Phys. Chem.*, 1925, **29**, 113, 540; M. Francis and F. P. Burt, *Proc. Roy. Soc. (London)*, A, 1927, **116**, 586. See Chapter III, page 48.

² The isotherm of D. O. Shiels for sulphur dioxide at 3 to 11 cm. pressure at 25° C. is far less curved than this (*J. Phys. Chem.*, 1929, **33**, 1178).

³ F. Durau, *Z. Physik*, 1926, **37**, 419. The glass was that used by G. C. Schmidt and F. Durau, *Z. physik. Chem.*, 1924, **108**, 128.

powder sorbed from the air 0.0276 g. in a few hours and 0.1617 g. in three months. Between experiments the powder was always re-evacuated at 570° C.

Such dry glass powder does not measurably sorb ¹ nitrogen, hydrogen or dry air at 18° C. Carbon dioxide is sorbed, but only to the extent of 16 per cent of a monomolecular layer at atmospheric pressure; this sorption is reversible and amounts to 0.059 c.c. (at N.T.P.) at atmospheric pressure. The value of n for carbon dioxide in the classical sorption isotherm is only one-third as great as with ordinary glass surfaces (see this chapter, page 241).

SORPTION OF VAPOURS

When the volume, density or compressibility, rate of reaction, etc., of a vapour is measured in glass vessels it is frequently necessary to take into account the amounts sorbed on the walls. Loomis and Smith ² summarize their observations in the statement: "At very low pressures the adsorption of nitrogen pentoxide on the walls of our Pyrex glass apparatus and the occlusion of oxygen as the heavier gases are condensed have been shown to involve a large fraction of the total amount of gas present." In other cases sorption is negligible.³

Crespi, Moles and Miravalles ⁴ have investigated these effects more fully. In table 39 are given the number of milligrams sorbed at atmospheric pressure on the walls of a litre vessel and the percentage of the total weight of vapour which this constitutes. They found the classical sorption isotherm applicable to their results, the volumes sorbed per square centimetre being equal to $kp^{1/n}$. Values for k and n are included in the table. However, the values given for k

¹ That is, not even 0.001 c.c. per 10,000 sq. cm.

² A. G. Loomis and D. F. Smith, *J. Am. Chem. Soc.*, 1928, **50**, 1864.

³ For example, sulphur vapour by fused silica or by pyrites, (L. d'Or, *J. chim. phys.*, 1930, **27**, 239).

⁴ M. Crespi and E. Moles, *Anales soc. españ. fís. quím.*, 1926, **24**, 210, 452; 1930, **28**, 448; E. Moles and M. Crespi, *Anales soc. españ. fís. quím.*, 1929, **27**, 529; M. Crespi, *Anales soc. españ. fís. quím.*, 1927, **25**, 25; 1929, **27**, 108; E. Moles and R. Miravalles, *Anales soc. españ. fís. quím.*, 1925, **23**, 223.

are those found for large bulbs, those for the same apparent surface of glass tubing and ampoules being only two-thirds as great. The glass in all cases had been drastically cleaned, and evacuated at room temperature. The higher value of 2 mg. for hydriodic acid, or an apparent thickness of 30–35 molecules, they ascribe to chemical reaction with the glass.

TABLE 39

Sorption of Various Vapours on the Walls of a Litre Vessel

Gas . . .	SO ₂	NH ₃	CH ₃ Cl	O ₂	CO ₂	C ₂ H ₄	CO	Air
mg. . . .	0.40	0.18	0.088	0.056	0.086	0.038	0.014	0.012
% error . .	0.013	0.025	0.0042	0.0042	0.0047	0.0033	0.0012	0.0010
$k \times 10^9$. .	380	71	3.8	0.65	9.3	—	1.03	0.94
n	2	4	1.67	1.5	(2)	—	2	2

SORPTION OF PERMANENT GASES

Langmuir ¹ experimented at the temperature of liquid air with a pile of 200 slightly bent microscope cover glasses which had been heated with concentrated sulphuric and chromic acids, washed, and evacuated at 300° C. for one hour. His experiments are confined to very low pressures not exceeding 100 bars (approximately 0.1 mm.). Sorption increased in the following order: oxygen, argon, nitrogen, carbon monoxide and methane. Carbon dioxide was the only one whose sorption was measurable at room temperature, and not more than 1 per cent of the surface could have been covered at that temperature. At —183° C. sorption was sufficient to cover only a small fraction of the apparent surface.

Zeise ² has very carefully repeated and extended Langmuir's experiments, using about 1,000 cover glasses separated by fibres of similar soft glass about 0.15 mm. thick. No details are given as to the cleaning of the glass but it had at least been in contact with water before being evacuated for two and one-half hours at 420° C. and another hour at a slightly higher temperature.

All of Zeise's results for low pressures at the temperature

¹ I. Langmuir and S. P. Sweetser, *J. Am. Chem. Soc.*, 1918, **40**, 1386.

² H. Zeise, *Z. physik. Chem.*, 1928, **136**, 385.

of liquid oxygen (90.0° abs.) are reproduced in fig. 84¹ which includes several series of measurements each for methane, nitrogen, oxygen and hydrogen expressed in the number of gram moles per square centimetre. The highest results obtained would be sufficient to cover 52 per cent of the apparent surface with a monomolecular layer of methane,

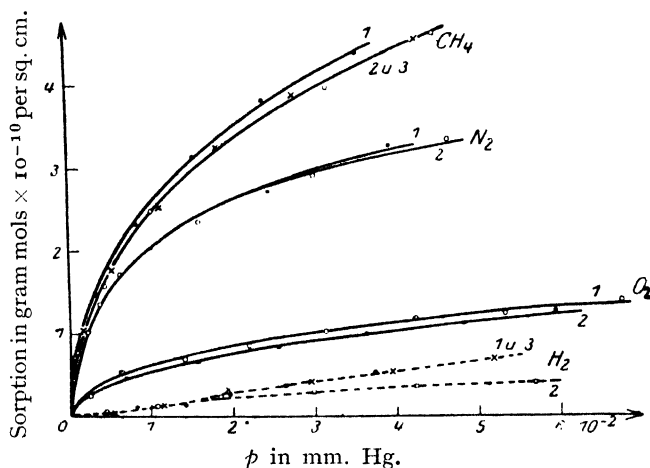


Fig. 84.—Zeise's Isotherms for the Sorption of Gases by Glass at 90° abs.

29 or 77 per cent with nitrogen, depending upon the calculation, 10 or 36 per cent with oxygen and much less with hydrogen.

A modification of the apparatus was necessary at higher pressures (4.5 to 307 mm.) on account of the inevitable error in the evaluation of the amount of gas in the dead space. Measurements were thus made with nitrogen at liquid air temperature and with methane and hydrogen at the temperature of a mixture of solid carbon dioxide with ether. The accuracy was probably sufficient to justify the author's conclusion that there is no indication that sorption exceeds

¹ H. Zeise, *Z. physik. Chem.*, 1928, **136**, 396, fig. 2.

a monomolecular layer. Johnson¹ likewise concludes from experiments with an electrodeless discharge tube that the amount of atomic hydrogen sorbed at saturation is less than would correspond to a complete monatomic layer.

In discussing the formation of hydrogen from hydrogen atoms at glass walls Polányi is said to have derived values for adsorption potentials equal to 1,500–4,000 gram calories for moist glass, for dry glass and "quartz" more than 4,500 gram calories, and for "metal" 40,000 gram calories.²

¹ M. C. Johnson, *Proc. Roy. Soc. (London)*, A, 1929, **123**, 610. For other experiments on sorption of ions and molecules in an electrodeless discharge tube, see V. L. Granovskii, *J. Russ. Phys.-Chem. Soc., Phys. Pt.*, 1929, **61**, 203.

² Mihály Polányi, *Chem. Rund. Mitteleuropa Balkan*, 1927, **4**, 160 (through Chemical Abstracts, 1929, **23**, 1341).

CHAPTER VIII

SORPTION BY IMPERMEABLE CRYSTALS ¹

SORPTION OF WATER VAPOUR BY QUARTZ AND FELDSPAR

Quartz possesses chemically inert surfaces ² so that sorption thereon, if measurable, should promise unusually simple and significant results. The difficulty is that in an original crystal of quartz the weight of the quartz is out of all proportion to the weight of any film sorbed thereon. Such sorption could only be measured by a very robust and exceedingly sensitive microbalance. Ihmori ³ attempted such direct weighings with an insufficiently sensitive microbalance. He used quartz

¹ The following information quoted from Chemical Abstracts, 1928, **22**, 3562, probably belongs in this chapter.

"Chromic chloride adsorbs water vapour, which causes a variable density of the product. The adsorption is analogous to that of gases on glass walls according to the equation $dx/dt = 1/(at + b)$. The amount of water adsorbed exceeds 0.5 molecule of water per molecule of chromic chloride, and molecular volume increases with increase in water adsorbed. Chromic chloride must be heated above 100° in a current of dry air to become dehydrated. Under such conditions it has a density of 2.916." (M. Crespi, *Anales soc. españ. fis. quim.*, 1928, **26**, 152.)

² P. G. Nutting (*Science*, 1930, **72**, 243) has shown that quartz surfaces can readily be made highly active by successive treatment with alkali and acid and heating, or by etching with hydrofluoric acid. K. Scheringa (*Pharm. Weekblad*, 1919, **56**, 94) reviews the literature upon sorption of water vapour and gases by powdered paraffin, sodium sulphate, sodium chloride, ammonium chloride, potassium chlorate, pumice, etc., and shows by his own experiments that this is usually not a source of error in gravimetric analysis. However, 50 g. of finely powdered potassium bromide sorbed 5 mg. of water vapour. See also Chapter VII, page 213, footnote 1.

³ T. Ihmori, *Wied. Ann. der Physik*, 1887, **31**, 1010. G. Ising and N. Urelius (*Kgl. Svenska Vetenskapsakad. Handl.*, (3), 1928, **6**, No. 4, p. 39) found appreciable sorption on a quartz pendulum even at low relative humidity.

crystals which had been ground and polished into the form of balance weights.

Ihmori found that when the five weights used had been cleaned only with a brush they took up measurable quantities of water from an atmosphere of high relative humidity. These amounts were much diminished by wiping the weights with leather; and after washing with water the apparent amounts, before correcting for the slight buoyancy due to the atmosphere of water vapour at 17°C ., became zero or negative in each case. After correction, they amounted to 43, 30, 60, 30 and 30 Å., respectively, in thickness. The sensitivity of the balance was possibly as high as 10 Å. The results became constant within five minutes.

In order to magnify the surface Briggs¹ used commercial crushed quartz, extracted with hydrochloric acid to remove the chlorides, carbonates and bicarbonates, and washed until the specific conductivity of the wash water was from 5 to 10×10^{-6} mhos. The powder was then dried at 110°C . and appeared to consist largely of sharp and angular grains with a diameter of from 0.005 to 0.05 mm. Their area was calculated on the assumption that they were cubes; that is, about 400 sq. cm. per gram.

Briggs had criticized the results of Dobeneck² on the ground that he had worked at or near the dew point with a powdered material that was not continually stirred. His own experiments were therefore carried out in rotating glass tubes whose surfaces were found to be scoured by the continuous action of the sharp quartz particles. The powder was exposed to air whose humidity was fixed by the presence of various solutions of sulphuric acid at 30°C . In the first experiments, the powder was first brought into equilibrium with the vapour and then its loss of weight was determined when it was exposed to an atmosphere dried by phosphorus pentoxide. The amounts removed were as follows after correcting for

¹ L. J. Briggs, *J. Phys. Chem.*, 1905, **9**, 628.

² A. von Dobeneck, *Forschungen auf dem Gebiete der Agrikulturphysik*, 1892, **15**, 163. Sorption of water vapour, carbon dioxide and ammonia on sand and pure powdered quartz.

the amount in the dead space and the amount sorbed by the glass walls by means of a blank experiment in which no powder was present :

Original p_{H_2O}	26.1	26.1	19.6	19.6	0.2	0.2	0.2
Mg. per 10,000 sq. cm.	4.7	4.4	2.2	2.4	0.2	0.1	0.5

In the next experiments the powder was first dried at 110° C., and a gain in weight was measured when the powder was exposed to the vapour from solutions of sulphuric acid at 30° C. The measurements were made at intervals up to 19 or 33 days.

p_{H_2O}	10.7	19.6	19.6	31.35	31.35
Time, in days	19	19	19	33	33
Mg. per 10,000 sq. cm.	2.3	5.9	5.6	27.4	25.9

The saturation pressure, p_s , at 30° is 31.51 mm. The powder showed a tendency in the latter part of the experiments at $p = 31.35$ mm. to stick to the walls of the tube, indicating capillary condensation. Finally, an automatic device for continuous tapping was attached and thereafter the weight remained constant.

From the first series Briggs calculated the thickness of the film of water to be 45 Å. where $p/p_s = 83$ per cent. From the second series, for $p/p_s = 99$ per cent, the thickness was calculated as 266 Å. In both cases this involved the assumption that no capillary condensation occurred, and no allowance was made for scratches or for fresh powder formed during the experiments.

Katz¹ employed quartz and anorthite (calcium aluminium silicate) synthesized at the Geophysical Laboratory in Washington by Dr. J. Day. They were finely powdered in an agate mortar until they passed through a sieve with eighty meshes per square centimetre. One milligram of quartz contained 140 million particles and 1 milligram of anorthite 120 million. Hence, if all the particles are assumed to be spheres, the minimum surface of 1 gram would be 3,260 sq. cm. and 3,150 sq. cm., respectively. The powder was exposed

¹ J. R. Katz, *Proc. Acad. Sci. Amsterdam*, 1912, 15, 1st part, p. 446.

above various solutions of sulphuric acid until the powder was at constant weight.

Katz's results ¹ are shown graphically in figs. 85 and 86. In fig. 85 the sorption, x/m , is plotted against relative humidity, p/p_s . The rise in x/m at high relative humidity is evidently due to capillary condensation of water in bulk. In fig. 86 the maximum thickness is plotted against the relative humidity.

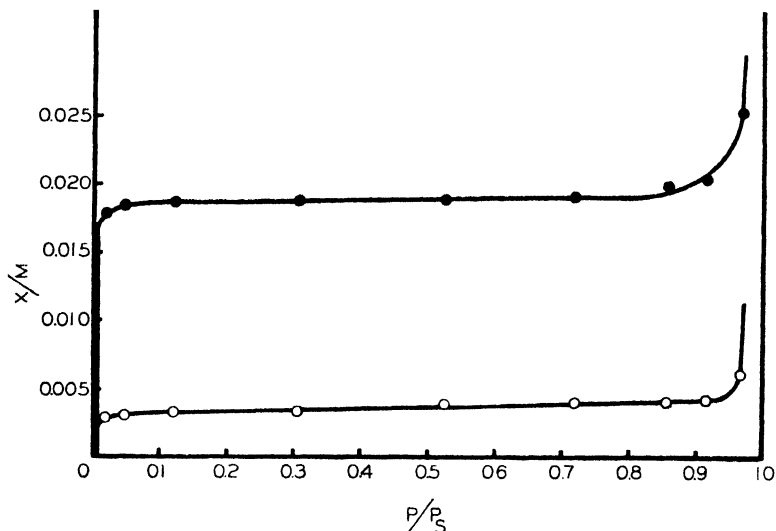


Fig. 85.—Katz's Isotherms for the Sorption of Water Vapour by Quartz and Anorthite. ○—Quartz; ●—Anorthite.

Katz takes his maximum thickness as 130 Å. for water on quartz and 620 Å. for water on anorthite. All of Katz's values for thickness have to be divided by four. Jones ² pointed out that Katz had made a numerical error but made one himself in correcting Katz. He also points out that Katz's results are much too large anyway because the particles cannot be spheres and cannot all be equal; finally, the attain-

¹ J. R. Katz, *Proc. Acad. Sci. Amsterdam*, 1912, **15**, 1st part, pp. 449 and 453.

² D. C. Jones, *J. Phys. Chem.*, 1925, **29**, 372.

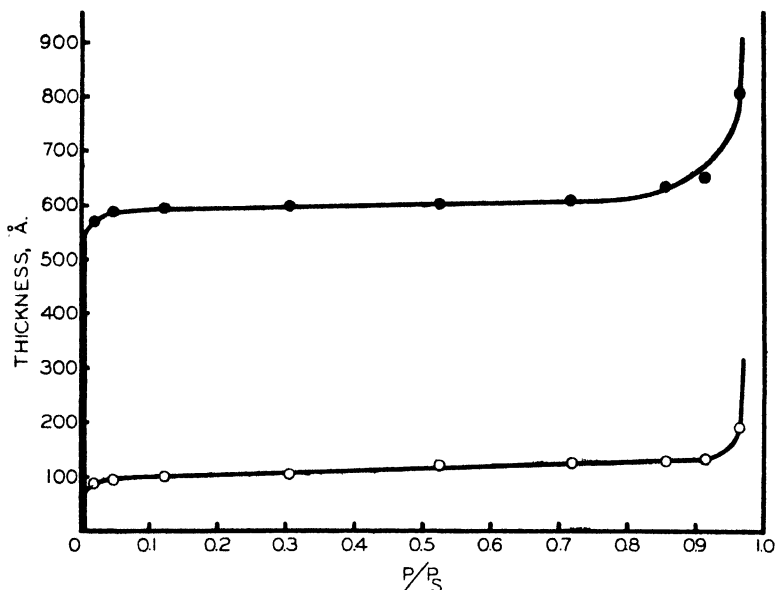


Fig. 86.—Katz's Isotherms for the Sorption of Water Vapour by Quartz and Anorthite. ○—Quartz; ●—Anorthite. Owing to a numerical error, Katz's values for the thickness are four times too great.

ment of true equilibrium by the method employed must have been very slow.

SORPTION OF GASES AND WATER VAPOUR BY MICA

Riess¹ showed that a fresh cleavage surface of mica condenses water vapour in a continuous transparent film and is wetted by water, whereas after standing exposed to the air the condensed film is mat and visible. Hence, a fresh leaflet of mica is not a good insulator, but after a few hours it becomes excellent because water vapour condenses upon the air film only in isolated droplets. Similarly, the path of an electric spark over such a dulled surface is made clear and conducting because a spark frees surfaces from sorbed films.

¹ P. T. Riess, *Die Lehre von der Reibungselektricität*, 1853, **2**, 220 (A. Hirschwald, Berlin, 1853); quoted by G. Quincke, *Pogg. Ann. der Physik*, 1859, **108**, 349.

In this connexion reference may be made to Quincke's¹ discussion of Wiedemann's observation² that when an electric spark strikes a point on the surface of a crystal, any powder thereon is scattered, leaving a clear ellipse whose long axis is parallel to the principal crystallographic axis and at right angles thereto with most optically positive crystals. Quincke concludes that this is an indication that the density of a sorbed film is different in different directions upon a crystal surface, being densest in the direction in which the density of the crystal itself is greatest. This conception would agree with that of Langmuir for cases in which the sorbed molecules constitute an extension of the space lattice of the crystal.

Cleavage planes of mica are 7.0 Å. apart, a distance equal to the thickness of the molecule.³

The only actual measurements of sorption on mica are careful ones due to Langmuir⁴ who worked at pressures up to 100 bars (approximately 0.1 mm.). As with glass, certainly not over 1 per cent of the surface was covered even with a single layer of molecules at room temperature independent of whether the mica had been previously heated or not.

Sheets of mica were separated by narrow strips of thin sheet iron previously heated to a bright red heat by dry hydrogen and they were held together by brass fasteners. The mica was heated for three hours at 300° C. It evolved 0.86 c.c. of water vapour (at 20° C. and 760 mm.) per 10,000 sq. cm. or enough water to cover the surface 2 molecules deep. However, the mica contains 18 per cent of combined water. Langmuir considers that the cleavage planes may be lined with combined water which upon exposure may adsorb a second layer. The amount of carbon dioxide simultaneously evolved was 0.24 c.c. per 10,000 sq. cm. or over three-quarters

¹ G. Quincke, *Pogg. Ann. der Physik*, 1859, **108**, 352.

² G. Wiedemann, *Pogg. Ann. der Physik*, 1849, **76**, 404; 1849, **77**, 534.

³ R. Marcelin, *Annales de physique*, 1918, **10**, 189; the corresponding distance for paratoluidine is between 5.0 and 5.5 Å. which may be two molecules, but more probably only one molecule thick.

⁴ I. Langmuir and S. P. Sweetser, *J. Am. Chem. Soc.*, 1918, **40**, 1376.

of that required for a monomolecular layer, together with 0.04 c.c. of nitrogen and some carbon monoxide from the iron strips.

Langmuir's data comprise measurements of sorption at the temperature of liquid air, using methane, carbon monoxide, nitrogen, argon and oxygen, methane being the most and oxygen the least sorbed. Experiments were also carried out with the same gases as well as carbon dioxide at -78°C . The amount of sorption at this temperature was only 5 to 20 per cent of that at the lower temperature. The data are not too accurate or reproducible, but within the experimental error they are represented by the Langmuir and not by the classical isotherm. Langmuir regards the data as showing that the sorption increases with pressure at first nearly linearly but at the higher pressures is approaching but not reaching saturation.

The Langmuir formula implies that a saturation value would ultimately be attained, and Langmuir compares the value in each case with that required to form a monomolecular layer. The saturation values so calculated as compared with the monomolecular requirement range from only 3 per cent for oxygen to 17 per cent for methane and 47 per cent for carbon dioxide at -78°C .; and at -183°C . from 11 per cent for oxygen to 86 per cent for methane. Thus in no case does the saturation value obtained by indefinite extrapolation equal a complete monomolecular layer. It seems highly probable that saturation values derived by direct experiment at much higher pressures would have been much less subject to temperature variation.

SORPTION OF AIR AND WATER VAPOUR BY SODIUM CHLORIDE ¹

The measurements of sorption of water vapour by rock salt may easily be completely distorted by the formation of

¹ Sorption upon salt should be exceptionally strong on account of the high surface tension as compared with, for example, water or mercury. J. E. Lennard-Jones and B. M. Dent (*Proc. Roy. Soc. (London)*, A, 1928, **121**, 258) find the following values for surface tension in dynes per cm.: NaCl 3000, NaF 5100, NaBr 2800, NaI 2350, KF 3200, KCl 2050, KBr 1950, and KI 1500.

a solution of the rock salt which, of course, is stable at a greatly reduced relative humidity as compared with that of pure water. This source of error is accentuated by the presence of small amounts of more soluble salts such as magnesium chloride. To the latter, Warburg and Ihmori¹ attribute all of the water film measured with their microbalance, at least to within their experimental error which corresponded to a thickness of 10 or 20 Å. The amounts observed had been apparently from 120 to 740 Å. deep on ground and polished surfaces of rock salt. Any roughness of the surface would still further lower the vapour pressure at which capillary condensation in bulk could occur.

Frazer² investigated the ellipticity of polarized light obtained by reflection from the surface. The ellipticity is ascribable to any departure from the assumption that the solid and vapour meet at a mathematical plane with no change in density or composition up to that plane. Ellipticity might be due to roughness, even that on a molecular scale due to thermal vibration, to sorption, or to any contraction of the material at the surface. Marked decrease upon heating, restored upon cooling, is clearly attributable to sorption. Frazer ascribed the different values obtained with fresh cleavage surfaces in air on evacuation and heating to sorption of air to a thickness not more than 6 Å. Ellipticity reached a minimum at 330° C., and above 400° C. volatilization of the sodium chloride caused fluctuations.

¹ E. Warburg and T. Ihmori, *Wied. Ann. der Physik*, 1886, **27**, 504.

² J. H. Frazer, *Phys. Rev.*, (2), 1929, **34**, 644. See Chapter II, page 26. See also the pioneer measurements of this kind made by P. Drude (*Wied. Ann. der Physik*, 1889, **36**, 536) and discussed by J. J. Haak and R. Sissingh (*Proc. Acad. Sci. Amsterdam*, 1919, **21**, 678). Drude demonstrated the thick layer of dirt which is put upon a surface by an attempt to clean it with leather or linen and points out that optically polished surfaces of every kind are rendered permanently unclean. In addition to rock salt, Drude studied fresh and contaminated cleavage surfaces of fluorspar, mica, calcite, gypsum, stibnite and galena, and with the latter investigated many methods of cleaning and polishing. Drude also showed that this method might be used for surfaces immersed in liquids, but his data have not been evaluated.

When a freshly cleaved crystal of rock salt was quickly put into a vacuum and thereafter exposed to the vapour of a saturated solution of sodium chloride, the readings showed no change, proving that the amount of water vapour sorbed is too small for detection. After evacuation at $350^{\circ}\text{C}.$, exposure to 5 mm. pressure of water vapour at $30^{\circ}\text{C}.$ produced a small but measurable effect which was found to be reversible and reproducible. Frazer demonstrated that a polished surface of salt, as distinguished from the cleavage surface just described, is attacked or altered by water vapour at a pressure much lower than that of a saturated solution of salt, as would indeed be expected.

Admirable care was taken by Durau¹ in the study and preparation of his specimens of sodium chloride for use in sorption. His intention of preparing sodium chloride entirely free from gases was frustrated by the necessary cost of using up silica tubing. Nevertheless, he evacuated the sodium chloride in the molten condition at $1,200^{\circ}\text{C}.$ where gases were still noticeably soluble, and afterwards ground the solid in an atmosphere of nitrogen. The gases thereby removed from 273 g. of sodium chloride amounted to (at N.T.P.) 53 c.c. of water vapour, weighing 43 mg., in addition to 7.4 c.c. of permanent gas consisting largely of carbon dioxide, carbon monoxide, possibly nitrogen and small amounts of hydrogen and methane. Some of these gases may have arisen from reaction between sodium chloride and the porcelain tube. Further quantities of gas and of water vapour were disengaged on evacuating the powder used in the sorption experiments at $480^{\circ}\text{C}.$, amounting to about 20 c.c. As will be seen, these amounts are ever so much greater than any of the measured amounts of sorption, and Durau argues plausibly that they come from the interior of the crystals upon heating.² In most cases there was no indication that the gases whose

¹ F. Durau, *Ann. der Physik* (4), 1928, **87**, 307.

² E. W. R. Steacie and G. B. Graham (*J. Phys. Chem.*, 1930, **34**, 2098) conclude that the solubility of water vapour in silica, alumina, potassium chloride and sodium sulphate at temperatures up to 900° is not greater than 0.00002 g. per gram of salt.

sorption was being measured could diffuse into the crystals at room temperature. Equilibrium was rapidly attained.

The amounts of sorption observed by Durau (at 18° C.) are calculated as c.c. at N.T.P. for 320.7 g. of powdered sodium chloride. The first experiments were carried out by

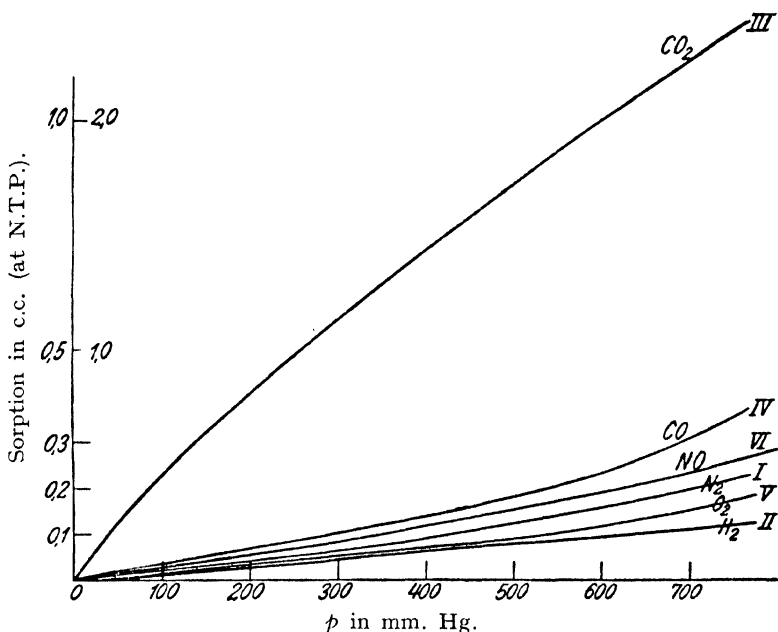


Fig. 87.—Durau's Isotherms for the Sorption of Gases by 320.7 g. of powdered Sodium Chloride. The scale of ordinates within the graph is for Carbon Dioxide only, that outside for all the other gases.

mere evacuation at room temperature without previous heating. The results for carbon dioxide are summarized in fig. 87,¹ in which it will be noted that the scale is halved for carbon dioxide in order to bring it within the diagram, which gives the results obtained with five other gases after evacuation at 480° C. This treatment did not alter the values for nitrogen,

¹ F. Durau, *Ann. der Physik* (4), 1928, **87**, 347, fig. 8.

whereas those for carbon dioxide were halved and the isotherm became a straight line, and the results for oxygen were doubled. Many details of the results were not completely cleared up and reference must be made to lengthy descriptions in the original paper; for example, experiments with carbon dioxide and with oxygen, followed by others with hydrogen in which water appeared to be formed, etc., etc. Other experiments with methane, ethane, propane, sulphur dioxide and nitrous oxide are given in fig. 88.¹ In none of these experiments is there enough sorption to cover more than a small fraction of the surface even 1 molecule deep. The sorption of the hydrocarbons was not measurable below a pressure of 200 mm.

Experiments with water vapour were unsuccessful but measurements were made with moist nitrogen, oxygen and carbon dioxide which increased the sorption of nitrogen and oxygen (three- to four-fold) and diminished that of carbon dioxide; thus again the amounts sorbed were far too small to cover the moist surface. Finally, after drying the powder, the sorption for nitrogen, and especially that for carbon dioxide, was found to have diminished. Durau concludes that the treatments had removed any specially active patches of surface by recrystallization to normal space lattice.

Disconcerting results were obtained by Herbert² when studying the sorption of ammonia and sulphur dioxide on sodium chloride and of ammonia on sapphire which he summarized in the following sentence. "In no experiment of reasonable duration (up to one month) could a sufficiently close approach to saturation be obtained to render extrapolation to the equilibrium value possible." His sodium chloride after purification was fused in a silica dish, powdered in an agate mortar and heated at 500° C. in vacuo until it sintered into a coherent porous mass. Had the particles remained separate, their apparent area would have been estimated as 2 sq. m., and the maximum amount of ammonia sorbed at nearly atmospheric pressure would have amounted to 2.3 c.c. per 10,000 sq. cm.

¹ F. Durau, *Ann. der Physik* (4), 1928, **87**, 360, fig. 10.

² J. B. M. Herbert, *Trans. Farad. Soc.*, 1930, **26**, 118.

The "sapphire" was powdered, boiled with hydrochloric acid, strong aqua regia, and water, and after ignition at 300°C . contained 98 per cent of Al_2O_3 . It was then heated

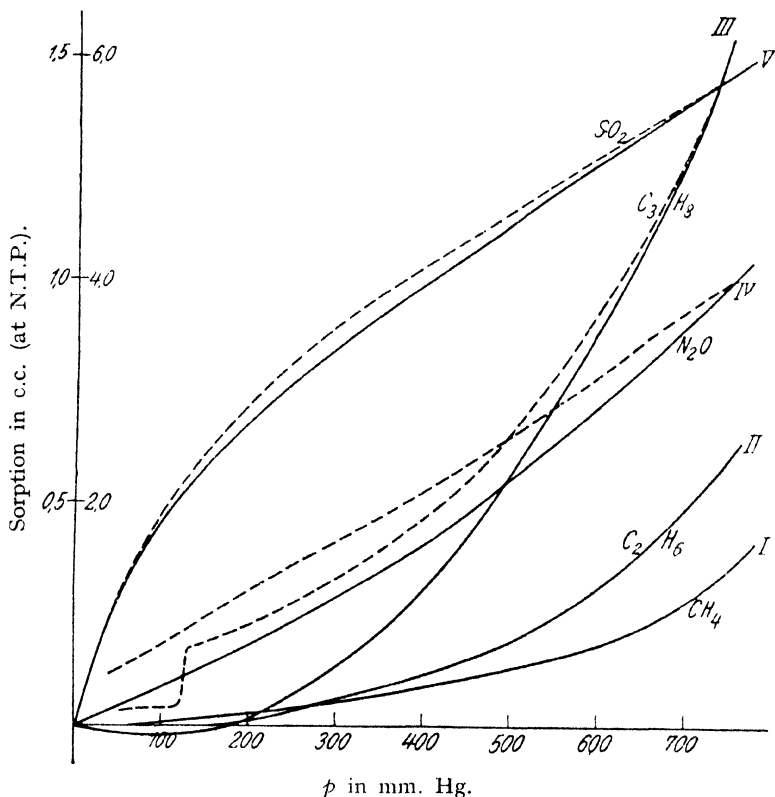


Fig. 88.—Durau's Isotherms for the Sorption of Gases by 320.7 g. of powdered Sodium Chloride. The scale of Ordinates within the graph is for Sulphur Dioxide only, that outside for all the other gases.

to 900°C . for four days, although water had been freely given off even at 600°C . The sintered solid mass was re-powdered and heated to 800°C . The sorptive power was now much less than that of the original powder.

SORPTION BY CALCIUM FLUORIDE

de Boer¹ utilized a lamp whose filament was coated with calcium fluoride which upon heating distilled onto the glass wall and there sorbed iodine vapour. The film of calcium fluoride is invisible but it becomes brown as it is exposed to higher pressures of iodine vapour. When the vapour is saturated, crystals of iodine appear on the glass and elsewhere.² In one publication he points out that "the surface of the CaF_2 -layer is often much larger than the area of the glass covered by it. Therefore it is impossible to determine the thickness of the layer", but elsewhere he considers that the area of the fluoride does not exceed that of the glass if there is only 0.2 mg. to 75 sq. cm. of glass. Here then the sorbed layer might be 30 molecules deep, if none is sorbed by the glass itself and the surface of the calcium fluoride is perfectly smooth and continuous. The rapid rise in sorption at high relative humidity, p/p_* (where p_* is now sublimation pressure of iodine), a rise which most authors would attribute to capillary condensation, was considered to be adsorption. The distinct difference in colour from that of ordinary iodine is ascribed to polarization of the sorbed iodine atoms.

SORPTION BY SUGAR

Sorption of air by sugar appears to be demonstrated in the intriguing experiment of Jaeckel³ carried out whilst investigating the cause of sugar dust explosions. When 200 g. of sugar was powdered in an air-tight mill, the pressure was diminished by 23 mm.

¹ J. H. de Boer, *Physica*, 1928, **8**, 145; *Verslag Akad. Wetenschappen Amsterdam*, 1928, **37**, 237; *Proc. Acad. Sci. Amsterdam*, 1928, **31**, 906.

² Compare the observations of Wulff, Chapter VII, page 237.

³ G. Jaeckel, *Z. Ver. deut. Zuckerind.*, 1923, **73**, 119.

CHAPTER IX

SORPTION BY METALS

OCCCLUSION AND DIFFUSION OF GASES IN METALS

The phenomena illustrated in connexion with sorption by metals are so exceptionally diversified in nature that an adequate account would require a discursive treatise and would lie outside the scope of this volume. However, it is possible to make reference to some of the actual measurements of sorption which have been carried out.¹

With the exception of liquid mercury, which will be discussed first, all the metals have been employed either in the insufficiently understood amorphous form or as conglomerates of crystal grains cemented together and often surprisingly permeable in effect. Metals are usually good solvents for gases,² and these frequently form chemical compounds which may remain in solution or may ultimately embrace the whole of the metal with the formation of such a product as Pd_3H_2 . Purity of metals is, of course, highly exceptional. Gold leaf,³

¹ Nearly 100 references to work on sorption in metals between 1834 and 1899, especially referring to hydrogen and oxygen, are given by E. Bose, *Z. physik. Chem.*, 1900, **34**, 710. This list was amplified and also brought up to the beginning of 1922 by L. W. McKeehan who listed 63 additional titles of papers dealing with hydrogen and palladium (*Phys. Rev.*, (2), 1923, **21**, 339). D. P. Smith (*J. Phys. Chem.*, 1919, **23**, 200) adds a classified list of papers dealing with the interaction of hydrogen and the various metals. Under each metal he has indicated such papers as contain bibliographies of earlier work upon that metal. The writer has not read a majority of these 242 papers, and those interested may be referred to these sources. E. Fritzman (*Zhur. Prikladnoi Khim.*, 1930, **3**, 455) lists 150 references.

² See S. Dushman, *J. Franklin Inst.*, 1931, **211**, 689. Noble gases do not dissolve in metals (A. Sieverts and E. Bergner, *Ber.*, 1912, **45**, 2576).

³ I. Griffith, *Bull. Wagner Free Inst. Sci. Philadelphia*, 1928, **3**, 59.

for example, may contain from 76 to 83 per cent of gold, 7 to 20 per cent of silver, and from 2 to 9 per cent of various base metals ; it may be fibrous or polycrystalline.

Ferrous alloys¹ may occlude as much as 200 times their own volume of gases ; of these hydrogen is the most readily extracted upon heating in vacuo, carbon monoxide next, while nitrogen is held most tenaciously. Studies of such phenomena were made by Graham² and later more systematically by Sieverts.³ He found that copper takes up hydrogen above

¹ G. Alleman and C. J. Darlington, *J. Franklin Inst.*, 1918, **185**, 161, 333 and 461. T. Graham (*Compt. rend.*, 1867, **64**, 1067 ; *Pogg. Ann. der Physik*, 1867, **131**, 151 ; *Chem. Zentr.*, 1867, **38**, 973) made the observation that meteoric iron contained 2.85 volumes of hydrogen, much more than wrought iron usually sorbs from hydrogen at one atmosphere pressure. For atomic hydrogen in iron nitride, see S. Satoh, *Nature*, 1931, **128**, 457.

² For example, T. Graham, *Phil. Mag.*, (4), 1866, **32**, 401 ; *Pogg. Ann. der Physik*, 1866, **129**, 549 ; *Chem. Zentr.*, 1867, **38**, 129. He asserts that palladium foil which was impermeable for dry hydrogen or air at room temperature was permeable for ether. L. A. Welo (*Phys. Rev.*, (2), 1918, **12**, 251) has found spectroscopically that the gases emitted by nickel, palladium, and platinum upon progressive heating are derived from carbon and oxygen, and their escape is related to the temperature ranges of high photoelectric emission ; at other temperatures (intermediate in the case of palladium) hydrogen is evolved. Silver and gold evolve hydrogen at all high temperatures, but carbon lines predominate at ranges of high photoelectric activity. Only after heating nearly to fusion is a good vacuum obtainable.

³ Some Sieverts measurements are included with those of others in *Landolt-Börnstein physikalisch-chemische Tabellen*, 1923, pp. 773-784, and in the appendix to A. Sieverts, *Z. Metallkunde*, 1929, **21**, 43. Other papers are : A. Sieverts, *Z. physik. Chem.*, 1907, **60**, 129 (H₂ by Cu, Fe, reduced Fe powder, Ni, Co, Ag and Pt ; N₂ by Fe and reduced Fe ; O₂ by Ag and Pt) ; 1911, **77**, 591 (H₂ by Ni, Cu and Fe) ; 1914, **88**, 103, 451 (H₂ by Pd wire, black, sponge, foil and liquid Pd) ; *Z. Elektrochem.*, 1910, **16**, 707 (CO by Cu, Ni and Fe ; CO₂ by Cu ; H₂ and N₂ by Fe, Ni, Co, Cu, Cd, Tl, Pb, Bi, Sn, Sb, Al, Ag, Au and Pd ; O₂ by solid and liquid Ag) ; A. Sieverts and E. Bergner, *Ber.*, 1911, **44**, 2394 (H₂ and N₂ by Ta and W) ; 1912, **45**, 2576 (A and He by liquid and solid Cu, Au, Ni, Fe, Pd, Al, Mg, U, Ta ; H₂ by U) ; *Z. physik. Chem.*, 1913, **82**, 257 (solubility of SO₂ in alloys of Cu with Au, Ag, Pt, and in oxygen and sulphur compounds of Cu) ; A. Sieverts and A. Gotta, *Z. anorg. allgem. Chem.*, 1928, **172**, 1 (H₂ by Ce, Pr and a Larich alloy) ; H. Hagen and A. Sieverts, *Z. anorg. allgem.*

400° C., the amount increasing with the temperature, but only a small amount of hydrogen is retained on cooling. Diffusion of hydrogen through a copper tube was appreciable at 640° C. Indeed, in general hydrogen diffuses readily through metals above 600°. In the case of iron, occlusion and diffusion of hydrogen became noticeable upon heating to 400° C., increasing rapidly with further rise of temperature.¹ Nitrogen was very slightly sorbed above 900° C. but was not given up by the iron at 500° C. even in vacuo, and diffusion was not observed even at 1,000° C. Reduced iron takes up large quantities of nitrogen above 900° C., but these are evolved again on cooling; however, the amounts taken up at still higher temperatures are less. This may be due to change in the iron.² Nickel³ takes up hydrogen even at 200° C., the amount increasing rapidly with rise of temperature. Diffusion

Chem., 1930, **185**, 225 (H₂ by Ge, In, Cb and Ti); A. Sieverts and J. Hagenacker, *Z. physik. Chem.*, 1909, **68**, 115 (H₂ and N₂ by molten Ag; O₂ by Ag); *Ber.*, 1909, **42**, 338 (H₂ by Ni); H. Huber, L. Kirschfeld and A. Sieverts, *Ber.*, 1926, **59B**, 2891 (H₂ by V and Ti); A. Sieverts and E. Jurisch, *Ber.*, 1912, **45**, 221 (H₂ by Pt wire and compact Pt; CO₂ and SO₂ by Pt; H₂ and CO₂ by Rh); A. Sieverts, E. Jurisch and A. Metz, *Z. anorg. allgem. Chem.*, 1915, **92**, 322 (H₂ by Pd alloyed with Pt, Ag and Au); L. Kirschfeld and A. Sieverts, *Z. physik. Chem.*, Abt. A, 1929, **145**, 227 (H₂ by Ti); *Z. Elektrochem.*, 1930, **36**, 123 (H₂ by V and V alloyed with Fe); A. Sieverts and F. Krüll, *Ber.*, 1930, **63B**, 1071 (N₂ by Fe); A. Sieverts and W. Krumbhaar, *Ber.*, 1910, **43**, 893 (N₂ by Al and Fe; CO₂ and SO₂ by Cu; CO by Cu and Ni; O₂ by Ag and Au, and by Ag alloyed with Au; H₂ by Cu, Ni, Fe, Pd, and by copper alloys); *Z. physik. Chem.*, 1910, **74**, 277 (N₂, CO₂, CO, SO₂ and H₂ with solid and liquid Cu, and O₂ with liquid Cu); A. Sieverts and G. Müller-Goldegg, *Z. anorg. allgem. Chem.*, 1923, **131**, 65 (H₂ by Ce and Ce alloys); A. Sieverts and E. Roell, *Z. anorg. allgem. Chem.*, 1925, **146**, 149 (H₂ by Ce, La mixed metals and Ce alloyed with Mg); 1926, **150**, 261 (H₂ by Pr and Nd); 1926, **153**, 289 (H₂ by Zr powder and Th).

¹ I. Langmuir (*J. Am. Chem. Soc.*, 1918, **40**, 1380) found that iron at room temperature almost instantaneously sorbs enough oxygen to form a monomolecular layer. Thereafter there is a slow consumption of oxygen, probably due to absorption (solid solution). None of the oxygen could be removed by evacuation or by heating.

² L. Kaul, *Metallbörse*, 1928, **18**, 1883.

³ A. Sieverts, *Z. Elektrochem.*, 1910, **16**, 707.

of hydrogen through a nickel tube is noticeable above 450°C . Although cobalt¹ begins to take up hydrogen above 700°C ., rising to 0.4 volumes at $1,000^{\circ}\text{C}$., neither cobalt nor nickel retains an appreciable amount of the gas upon cooling. Hydrogen diffuses through the walls of a platinum tube above 576°C . but the actual amounts within the metal are very slight.² Oxygen did not diffuse through silver at this temperature.

Sieverts' work may be summarized in part as follows: Helium and argon are not sorbed by copper, gold, nickel, iron, palladium, aluminium, magnesium, uranium and tantalum, whether solid or molten. Hydrogen is sorbed by uranium ($1,100^{\circ}\text{C}$.), copper (above 400°C .), iron (400° – 850°C .), nickel (above 200°C .), cobalt (above 700°C .), platinum (very slight at 576°C ., appreciable above $1,340^{\circ}\text{C}$.), tungsten ($1,500^{\circ}\text{C}$.), sorption increasing with temperature (except for iron) and very little hydrogen being retained on cooling to room temperature. Hydrogen and nitrogen are not sorbed by silver, cadmium, thallium, lead, bismuth, tin, antimony, aluminium, gold, zinc or rhodium, nor is nitrogen soluble in copper, nickel and palladium. Hydrogen is sorbed by the rare earth metals and the titanium and vanadium series (see this chapter, page 294, fig. 94, and pages 303 and 304, figs 98 and 99). Oxygen is not sorbed by gold, nor are carbon dioxide and carbon monoxide by copper. Carbon monoxide is sorbed by nickel and iron above $1,000^{\circ}\text{C}$. Carbon dioxide is not sorbed by rhodium or platinum. Sulphur dioxide dissolves freely in liquid copper but is not sorbed by solid copper or platinum.

Very thorough studies of the diffusion of oxygen through silver have been carried out by Johnson and Larose.³ They found the diffusion easily measurable between 352° and 607°C . For example, at 580°C . 124 c.c. (at N.T.P.) of oxygen passed through a square metre of silver plate 0.3 mm. thick per hour.

¹ A. Sieverts, *Z. physik. Chem.*, 1907, **60**, 129; compare this chapter, page 309, footnote 1.

² S. von Wroblewski, *Wied. Ann. der Physik*, 1879, **8**, 29.

³ F. M. G. Johnson and P. Larose, *J. Am. Chem. Soc.*, 1924, **46**, 1377; 1927, **49**, 312.

Commercial silver contains large amounts of oxygen ¹ which is difficult to remove completely by evacuation even in the molten condition. The sprouting and momentary luminescence of silver upon solidification is common knowledge. Platinum and palladium show similar tendencies.² The molten silver contains 100 volumes of oxygen (23 volumes at N.T.P.) when exposed to one atmosphere pressure of oxygen. This diminishes slowly with further rise of temperature until at 1,125° C. it is 19.5 volumes (at N.T.P.). Almost the whole of this oxygen is suddenly evolved upon solidification, leaving only 0.6 volumes (at N.T.P.) in the solid silver.

Even more striking is the sudden change in the amount of nitrogen taken up by powdered iron above and below 900°. Nitrogen is sorbed in the solid powder just above 900° to the extent of 0.022 per cent ³ by weight, diminishing slowly in this solid with rise of temperature just like oxygen in liquid silver. On cooling below 900° C. concurrently with the transition from the α to the β iron, practically all of this nitrogen is evolved; that is, above 900° iron may contain 1.37 volumes (at N.T.P.), below 900° C. not over 0.1 volumes.

Sieverts, like Deming and Hendricks,⁴ found that the copper tubes used for diffusion became brittle and fissured in an atmosphere of hydrogen. Lombard ⁵ showed that the diffusion increased rapidly even when the temperature and pressure were held constant. The copper used by Hendricks and Ralston ⁶ was 99.900 per cent pure before the oxidation by

¹ F. Durau, *Ann. der Physik* (4), 1928, **87**, 320; *Z. Physik*, 1926, **37**, 441.

² L. Kaul, *Metallbörse*, 1928, **18**, 1883; iron, nickel, cobalt, copper and platinum do the same in hydrogen (A. Sieverts, *Z. Metallkunde*, 1929, **21**, 40).

³ Electrolytic iron may take up as much as 0.06 per cent by weight of nitrogen between 900° and 1000° C. (A. Sieverts, *Z. Metallkunde*, 1929, **21**, 38).

⁴ H. G. Deming and B. C. Hendricks, *J. Am. Chem. Soc.*, 1923, **45**, 2857; W. E. Deming (*Phil. Mag.*, (7), 1928, **5**, 1081) has studied the diffusion of hydrogen through iron.

⁵ V. Lombard, *J. chim. phys.*, 1928, **25**, 590; for data and graphs for nickel and hydrogen, see *Compt. rend.*, 1923, **177**, 116.

⁶ B. C. Hendricks and R. R. Ralston, *J. Am. Chem. Soc.*, 1929, **51**, 3278.

phosphorus. They found that the specific diffusion of hydrogen in milligrams per square metre of surface per millimetre thickness of metal per hour was 17 at 497° C., 29 at 568° C., and 58 at 632° C. Meanwhile there was a decided increase in the size of the crystal grains. They rejected the explanation that the increase in size of intercrystalline cracks was due to reduction and attributed it to larger crystalline planes of cleavage, extending until they became mechanical openings or fissures, rendering the copper more permeable and brittle. Zinc, on the other hand, showed a decrease in crystalline size upon heating in hydrogen, while nickel remained unchanged. The specific diffusion of hydrogen through zinc was 8 at 305° C. and 32 at 373° C. With nickel, the specific diffusion increased from 34 at 478° C. to 369 at 798° C., all these results referring to one atmosphere pressure of hydrogen.

Importance attaches to the findings of Berliner¹ because it is customary for investigators to free metals from dissolved and occluded gases by heating to redness in vacuo. Berliner showed in experiments on platinum, palladium and copper that the metals sputter (*zerstäuben*) when giving up occluded gases such as air, hydrogen or carbon dioxide, as is shown by the blackening of adjacent surfaces as in an incandescent lamp. Presumably carbon filament lamps are blackened partly by the same mechanism. It is evident that a smooth metallic surface could no longer be considered perfect after such treatment.

The specific diffusion is proportional to the square root of the pressure as well as to a high power of the absolute temperature, such as 14.6 in the case of oxygen and silver.² Richardson³ developed a formula for the diffusion constant D of a gas through a metal $D = KP^{\frac{1}{2}}T^{\frac{3}{2}}e^{-\frac{q}{4T}}$ where P

¹ A. Berliner, *Wied. Ann. der Physik*, 1888, **33**, 289.

² F. M. G. Johnson and P. Larose, *J. Am. Chem. Soc.*, 1924, **46**, 1377; 1927, **49**, 312; where many references to previous work may be found.

³ O. W. Richardson, *Phil. Mag.*, (6), 1904, **7**, 266; O. W. Richardson, J. Nicol and T. Parnell, *Phil. Mag.*, (6), 1904, **8**, 1 (measurements of diffusion of hydrogen through platinum).

and T are the pressure and temperature, K is a constant and q is the heat of dissociation of the gas into single atoms within the metal. The estimated values of q are found to be much smaller than the heats of dissociation in the gaseous state, which may well be accounted for by the positive heat of sorption. Richardson's equation applies as far as tested to the diffusion of hydrogen, nitrogen and carbon monoxide through steel ⁴ and of hydrogen through platinum.¹

THE ACTIVATION OR ELECTRIFICATION OF DESORBED GASES

The sorption of oxygen by silver ² at high temperatures, of sulphur dioxide by copper and its alloys,^{3,4} of nitrogen

¹ H. M. Ryder, *Elec. J.*, 1920, **17**, 161. S. von Wroblewski (*Wied. Ann. der Physik*, 1879, **8**, 29) calculated from Graham's earlier data that at a red heat iron contained four times its own volume of carbon monoxide and less of hydrogen, their respective diffusion coefficients being 0.00000002 and 0.00000054 cm.²/sec. Platinum at red heat contained 0.17 of its volume of hydrogen, whose diffusion coefficient was 0.00053 cm.²/sec. T. Graham found at room temperature 0.1 to 0.2 volumes of hydrogen in platinum wire, 3.8 to 5.5 in an old crucible, 2.3 to 2.8 in an old tube and 1.48 volumes in platinum sponge (*Phil. Trans. Roy. Soc. London*, 1866, **156**, 399; also *Chem. and Phys. Researches*, 1876, p. 263). L. Mond, W. Ramsay and J. Shields (*Phil. Trans. Roy. Soc. London*, A, 1895, **186**, 658) found 0.4 volumes of gas in platinum foil at room temperature extracted by evacuating at red heat. Of this three-fourths was carbon dioxide and one-fourth was not absorbed by alkaline pyrogallol solution.

² E. W. R. Steacie and F. M. G. Johnson, *Proc. Roy. Soc. (London)*, A, 1926, **112**, 542; compare A. Sieverts, *Z. physik. Chem.*, 1907, **60**, 129. A. F. Benton and J. C. Elgin (*J. Am. Chem. Soc.*, 1929, **51**, 7) found it independent of temperature and pressure at the low temperatures 100° and 110° C. They assumed that the strong sorption under these conditions might be due to a monomolecular layer on the exterior. Under the same conditions hydrogen was not measurably sorbed, and water vapour was much more sorbed in the presence of oxygen than in the presence of hydrogen. On the other hand, F. Durau (*Z. Physik*, 1926, **37**, 445) found hydrogen appreciably sorbed at 18° C., the amounts sorbed being somewhat less than proportional to the pressure; the sorption of nitrogen was not quite completely reversible, and that of air much less reversible. The better the outgassing of the silver filings, the less the sorption of air at room temperature became.

³ A. Sieverts and E. Bergner, *Z. physik. Chem.*, 1913, **82**, 257.

⁴ A. Sieverts and W. Krumbhaar, *Z. physik. Chem.*, 1910, **74**, 277.

by iron,¹ and of hydrogen by platinum,² nickel,³ copper,⁴ iron,⁵ cobalt,⁶ silver,⁷ or tantalum⁸ is proportional to the square root of the pressure. Johnson and Larose are of the opinion that the atoms of a gas dissolved in the metal combine successively with the metallic atoms of the space lattice, forming unstable compounds which, in the intervals of dissociating and recombining with metal atoms further inside the metal, may be regarded as ions. A more general view appears to the writer to be that dissolved gases, whether molecules or not, will to a certain proportion unite with the free electrons that pervade a metal, and that diffusion of both charged and uncharged atoms or molecules of the gas will occur. Then when the diffusing ions reach the farther surface, or are desorbed at the original surface, some may escape into the gaseous atmosphere before they have lost their charge.

These explanations may, as Johnson and Larose suggest, account for

“the charge that gold takes in hydrogen or oxygen,⁹ the dissociation of hydrogen in the presence of a heated filament,¹⁰ the activity of hydrogen in the diffusion experiments of Ramsay,¹¹ work on electromotive force of gas cells,¹² the fact that hydrogen evolved by a fresh cathode in a vacuum tube obeys Faraday's laws,¹³ and the transparency of thin sheets of silver when heated

¹ A. Sieverts, *Z. physik. Chem.*, 1907, **60**, 129; E. Jurisch, *Dissert.*, Leipzig, 1912; H. Hagen, quoted by A. Sieverts, *Z. Metallkunde*, 1929, **21**, 38.

² O. W. Richardson, J. Nicol and T. Parnell, *Phil. Mag.*, (6), 1904, **8**, 1; A. Sieverts and E. Jurisch, *Ber.*, 1912, **45**, 221.

³ A. Sieverts and J. Hagenacker, *Ber.*, 1909, **42**, 338.

⁴ A. Sieverts and W. Krumbhaar, *Z. physik. Chem.*, 1910, **74**, 277.

⁵ B. Neumann, *Stahl und Eisen*, 1914, **34**, 252.

⁶ A. Sieverts, *Z. physik. Chem.*, 1907, **60**, 129.

⁷ A. Sieverts, *Z. Metallkunde*, 1929, **21**, 39; E. W. R. Steacie and F. M. G. Johnson, *Proc. Roy. Soc. (London)*, A, 1928, **117**, 662.

⁸ A. Sieverts and E. Bergner, *Ber.*, 1911, **44**, 2394.

⁹ H. Hartley, *Proc. Roy. Soc. (London)*, A, 1914, **90**, 61.

¹⁰ I. Langmuir, *J. Am. Chem. Soc.*, 1915, **37**, 417.

¹¹ W. Ramsay, *Phil. Mag.* (5), 1894, **38**, 206.

¹² E. Bose, *Z. physik. Chem.*, 1900, **34**, 701.

¹³ C. A. Skinner, *Phil. Mag.*, (6), 1906, **12**, 481.

in an atmosphere of oxygen,¹ the latter fact being easily explained if one assumes that the oxygen takes up electrons on absorption."

Anderson² showed that hydrogen immediately after desorption from platinum or palladium is not only partly ionized but is also chemically more active than ordinary hydrogen, as is shown by its action upon sulphur and cupric oxide. He considered it improbable that this could be ascribed to the presence of ordinary atomic or triatomic hydrogen since the former would have been removed by glass wool and the latter would have altered the refractive index as measured in a sensitive interferometer. Venkataramaiah and Swamy,³ whilst finding agreement with Anderson's results, ascribe them to triatomic hydrogen. This would likewise seem to be a possible product when ionized atomic hydrogen escapes into an atmosphere of hydrogen. Venkataramaiah⁴ obtained active hydrogen by the surface combustion of hydrogen and oxygen on platinum, and by heating hydrogen in arcs of various metals. It is likewise produced when oxygen burns in an atmosphere of hydrogen, owing to ionization by the electrons emitted in the flame.

Polyakov⁵ discusses various possibilities of activation such as that only one atom of a molecule touches and is held by a palladium surface, liberating the other at the expense of the heat of sorption. The studies of Finch and Stimson⁶ on the electrification of gold, silver, nickel and platinum when heated in vacuo or in contact with oxygen, hydrogen, their mixtures, water vapour, carbon dioxide, carbon monoxide, nitrogen and argon have shown that the surface may be made either positive or negative and suggest that a rearrangement of the surface

¹ The reference given by Johnson and Larose is erroneous.

² P. Anderson, *J. Chem. Soc.*, 1922, **121**, 1153.

³ Y. Venkataramaiah and M. V. N. Swamy, *Proc. Sci. Assoc. Mahara-jah's College, Vizianagram*, December 1922, p. 23.

⁴ Y. Venkataramaiah, *J. Am. Chem. Soc.*, 1923, **45**, 261.

⁵ M. V. Polyakov, *Ber. Ukrain. wiss. Forsch.-inst. physik. Chem.*, 1929, **2**, 55; through *Chemical Abstracts*, 1930, **24**, 4434.

⁶ G. I. Finch and J. C. Stimson, *Proc. Roy. Soc. (London)*, A, 1927, **116**, 379; 1928, **120**, 235; 1929, **124**, 356.

atoms of the metal may be brought about. They suggest five different degrees or kinds of adsorption ranging from purely physical to truly chemical bonding.

The papers of Langmuir ¹ provide a model for the lucid and exact analysis of the electrical effects which accompany sorption and desorption. They are referred to independently measurable physical constants, such as electron affinity and ionization potential, and to universal relations, enabling a prediction of the extent of the effects of various factors to be made and supplying a guide to their experimental test and control.

In 1923 it was shown by Langmuir and Kingdon ² that a tungsten filament heated above 925° C. converts all caesium atoms which strike it into caesium ions. This is ascribed to the electron affinity of tungsten (Richardson work function) being 4.53 volts, while the electron affinity (ionizing potential) of a caesium atom is only 3.88 volts. When the work function for the filament was lowered to 2.69 volts by allowing a monatomic layer of thorium atoms to diffuse out upon the surface from thoriated tungsten, the positive ion emission became negligible. The tungsten surface may remain partly covered by caesium atoms and by other caesium atoms which have become ions, the balance depending upon the temperature.

A tungsten filament coated, by exposure to oxygen, with a monatomic film of oxygen ions which does not evaporate appreciably below 1,325° C. exhibits a work potential of 9.2 volts and therefore upon this surface all atoms such as those of copper, which have lower ionizing potentials, can be converted into positive ions.³ Caesium ions are then held much more firmly than by tungsten itself. The electron emission may under suitable conditions be increased a million-fold by

¹ For example, I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc. (London)*, A, 1925, **107**, 61 (caesium on tungsten, also oxygen-coated and thorium-coated tungsten); I. Langmuir and D. S. Villars, *J. Am. Chem. Soc.*, 1931, **53**, 486 (oxygen-coated tungsten sorbing caesium).

² I. Langmuir and K. H. Kingdon, *Science*, 1923, **57**, 58, *Proc. Roy. Soc. (London)*, A, 1925, **107**, 61; K. H. Kingdon and I. Langmuir, *Phys. Rev.*, (2), 1923, **21**, 380.

³ K. H. Kingdon, *Phys. Rev.*, (2), 1924, **23**, 774, 778.

the presence of the oxygen holding the cæsium.¹ The cæsium itself may have already increased the electron emission to many billion-fold that of pure tungsten. This affords a sensitive method of detecting the presence of oxygen in a gas. Further analysis and calculation yield a quantitative account of the ionization of atoms by such surfaces, relating the positive ion and electron emissions with the thermal ionization of cæsium vapour and the Saha equation.

The minimum temperature of thermionic emission from surfaces of platinum and thoriated tungsten is found by Srikantan² to be the same as that required to initiate the interaction of hydrogen with carbon dioxide on these surfaces. From this and other reactions it is concluded that the activation of gases at a catalytic surface is to a large extent influenced by the capacity of the surface to emit electrons at that temperature.

A recent and highly competent discussion of the subject of thermionic emission has been provided by Dushman,³ including detailed consideration of the effects of monatomic films of thorium on tungsten, of other rare earth metals and barium on tungsten and molybdenum, of cæsium on tungsten and oxidized tungsten, and of oxide-coated cathodes.

In this general connexion it is interesting to recall McBain's⁴ experiments on the sorption of hydrogen by charcoal at liquid air temperature and the time effects observed. A part of these may have been due to the conversion of sorbed hydrogen into the activated form which yields parahydrogen as studied

¹ I. Langmuir and D. S. Villars, *J. Am. Chem. Soc.*, 1931, **53**, 486.

² B. S. Srikantan, *Indian J. Phys.*, 1930, **5**, 685 (other references and activation of hydrogen and carbon dioxide). This indorses the statement of I. Langmuir (*J. Am. Chem. Soc.*, 1916, **38**, 2279): "The following experimental evidence shows, in fact, that there is a remarkable parallelism between the electron emission and the catalytic activity of a filament" (oxygen, nitrogen, water, thorium, and carbon from methane or cyanogen on tungsten).

³ S. Dushman, *Reviews of Modern Physics*, 1930, **2**, 381.

⁴ J. W. McBain, *Phil. Mag.*, (6), 1909, **18**, 916; *Z. physik. Chem.*, 1909, **68**, 471.

by Bonhoeffer.¹ Taylor and Sherman² show that a highly active nickel catalyst on kieselguhr at liquid air temperature is as effective as charcoal. Oxide catalysts are ineffective until from 0° C. upwards the hydrogen is sorbed in activated as distinguished from ordinary molecular form.

ADSORPTION ON LIQUID MERCURY

Owing to the very high surface tension of mercury, it is a matter of extreme difficulty to prepare and study a clean mercury surface. For example, it has been stated by different authors that air may raise the surface tension by as much as 100 dynes, may leave it unaffected, or may diminish it slightly. Evidently a surface of mercury lends itself with exceptional readiness to contamination by traces of grease, vapours, or any materials which can be derived from its surroundings.³

Several authors have applied the optical method to the determination of the thickness of the adsorbed layer of gas upon a mercury surface (compare the application of this method, described in Chapter II, page 26, to surfaces of glass, Chapter VII, page 231; and of sodium chloride, Chapter VIII, page 253). Haak⁴ concluded from measurements in vacuo and in the presence of air that the air sorbed on liquid mercury is about 16 Å. or 5 molecules deep, the sensitivity of the method being perhaps 1.3 Å. Reeser⁵ found the thickness

¹ K. F. Bonhoeffer and P. Harteck, *Naturwissenschaften*, 1929, **17**, 182, 321; *Sitzb. preuss. Akad. Wiss.*, 1929, p. 103; *Z. physik. Chem.*, Abt. B, 1929, **4**, 113.

² H. S. Taylor and A. Sherman, *J. Am. Chem. Soc.*, 1931, **53**, 1614.

³ For the disturbing effects in studying films upon mercury, see, for example, R. G. Mitton, *Trans. Proc. Roy. Soc. S. Australia*, 1929, **53**, 267.

⁴ J. J. Haak, *Dissertation*, Amsterdam, 1918; *Arch. Néerland. Sci.*, Series III A, 1923, **6**, 198; *Physica*, 1922, **2**, 12; *J. Inst. Metals*, 1923, **30**, 421; J. J. Haak and R. Sissingh, *Verslag Akad. Wetenschappen Amsterdam*, 1918, **27**, 417; *Proc. Acad. Sci. Amsterdam*, 1919, **21**, 678.

⁵ C. A. Reeser, *Dissertation*, Amsterdam, 1921; *Arch. Néerland. Sci.*, Series III A, 1923, **6**, 225; *Physica*, 1922, **2**, 135; C. A. Reeser and R. Sissingh, *Verslag Akad. Wetenschappen Amsterdam*, 1921, **30**, 151; *Proc. Acad. Sci. Amsterdam*, 1922, **24**, 102, 108.

of the adsorbed air layer to be between 17 and 28 Å. deep, whereas an adsorbed oil layer was between 11 and 22 Å. deep. Ellerbroek¹ found that mercury, after contact with dry air for about 20 hours, is covered by a layer 60 Å. deep and in contact with hydrogen, 20 Å. deep. Upon heating, the adsorbed layer becomes less, until it falls below the limit of observation (7 Å.). Hence, at first sight, the same method and materials give three results; namely, 16, 22 and 60 Å. deep for air at room temperature and pressure. These results gain in significance upon more careful examination. They are interpreted by the authors as being at variance with the Langmuir conception of adsorption and with the dipole explanation of the forces involved. However, the writer would place upon them a very different interpretation.

To begin with, the authors assume with Quincke² that the density of the air in actual contact with the mercury is 13.6, like that of the mercury itself, and they therefore assume a mean refractive index of 2.52 for the sorbed layer of air in calculating the thickness from the ellipticity observed. The experiment therefore proves that there is a substantial amount of material of some sort present. However, to the writer it is inconceivable that the forces of sorption could compress air to any such density. The writer suggests instead that it is a scum of mercuric oxide. This is borne out by the observations of Reeser on the restored azimuth which gives directly the value of refractive index of the sorbed layer without any complication of the question of thickness and is thus experimentally found to have values between 3 and 6; that is far too great even for the remarkable assumption as to the density of air but quite natural for a compound of mercury.

A fact of essential importance has not been mentioned; namely, that the sorbed layer appears very slowly, requiring a day or more for completion to the values cited above. Haak used the formula for monomolecular rate of reaction to follow the changes during the first eight hours. This slow rate was adduced as being incompatible with the Langmuir conceptions

¹ J. Ellerbroek, *Arch. Néerland, Sci.*, Series III A, 1927, **10**, 42.

² G. Quincke, *Pogg. Ann. der Physik*, 1859, **108**, 349.

which would require a fraction of a second for sorption to be complete. However, the writer would point out that it is still less compatible with the classical conception of a thick compressed film which would be formed much more nearly instantaneously than a Langmuir film, the gaseous atmosphere merely having to settle bodily towards the surface, about as fast as a gas rushing into a vacuum. Furthermore, it is of vital significance that the optical effects observed by Haak, Reeser and Ellerbroek are not to the slightest degree affected or reversed by evacuation at room temperature for eight hours, using a Gaede mercury pump. This accords with chemical combination such as the formation of a scum of mercury compounds upon the surface but not with the reversible equilibrium between free gas and the gas within the range of attraction of the solid.

The film on the mercury was less in the case of hydrogen, but hydrogen contains oxygen or other impurities. On warming this film in hydrogen to about 160° C. it disappeared.¹ Occasionally this occurred even with the film in air. Ellerbroek² himself once suggests that air perhaps produces an oxidation. Moist air containing carbon dioxide has a greater effect than dry air.

Another method of approach to the problem of sorption on mercury is to compare the radius of ultramicroscopic particles of mercury as deduced from the laws of Stokes or Stokes-Cunningham with that expected, and to ascribe any discrepancies to an adsorbed film of sufficient thickness to restore agreement. König³ found that with mercury particles of sufficient magnitude the movement in an electric field showed agreement with that calculated from the accepted value of the electronic charge and the movement under the influence of gravity. When the radius, as deduced from the rate of fall, fell below a certain value, the corresponding values for the electronic charge likewise diminished rapidly as much as four- or five-fold. This began when the calculated radius

¹ J. Ellerbroek, *Arch. Néerland. Sci.*, Series III A, 1927, **10**, 69.

² J. Ellerbroek, *Arch. Néerland. Sci.*, Series III A, 1927, **10**, 70.

³ M. König, *Z. Physik*, 1922, **11**, 253.

was less than 2,100 Å. in an atmosphere of carbon dioxide or 1,200 Å. in air. It is evident that very thick layers of adsorbed gas, amounting to many hundreds of Å. in depth, would be required to account for a five-fold change in the electronic charge by thus correcting the radius of particles whose apparent radius was about 500 Å. The writer considers that the true explanation is quite different, and that it is extremely unlikely that the mercury particles consisted of single independent droplets, because the investigations of Whytlaw-Gray¹ and others have demonstrated the extraordinary tendency of smokes and aerosols to form much larger secondary particles.

The sorption of a gas by liquid mercury amounts only to a monomolecular layer, 4 Å. deep, according to the direct measurements of Oliphant and Burdon.² The arrangement of their very ingenious and effective apparatus is shown in fig. 89.³

"Mercury from the reservoir A, maintained at a constant level H, is delivered through a regulating tap T_1 to the stainless steel nozzle N fastened over the end of the glass tube with sealing wax. This nozzle is perforated with 25 holes, each of which delivers about 20 drops per second. These drops fall down the tube F [about 50 cm. long] and collect in a pool at the bottom, whence the mercury flows out through the siphon S, finding its way through P_1 to the pump which returns it to the reservoir."

Through the side tube at F is fed a slow constant stream of hydrogen or of argon containing a small percentage of carbon dioxide. The stream of gases divides at the centre, half passing upward and half down, thence through Q_1 and Q_2 to the two tubes of a Rayleigh interferometer. Any gas adsorbed by the falling drops is given up at the bottom of the tube, causing an increase in the concentration of the carbon dioxide in the lower tube and a corresponding decrease in the upper tube. The number of drops is counted with a stroboscope.

¹ R. Whytlaw-Gray, J. B. Speakman and J. H. P. Campbell, *Proc. Roy. Soc. (London)*, A, 1923, **102**, 600.

² M. L. Oliphant, *Phil. Mag.*, (7), 1928, **6**, 422; M. L. Oliphant and R. S. Burdon, *Nature*, 1927, **120**, 584.

³ M. L. Oliphant, *Phil. Mag.*, (7), 1928, **6**, 427, fig. 1.

The number of molecules of carbon dioxide adsorbed per square centimetre of mercury surface was 6×10^{14} from argon containing 5 or 10 per cent of carbon dioxide and 5×10^{14} from argon containing 15 per cent of carbon dioxide. Using hydrogen as the indifferent gas, the carbon dioxide adsorbed

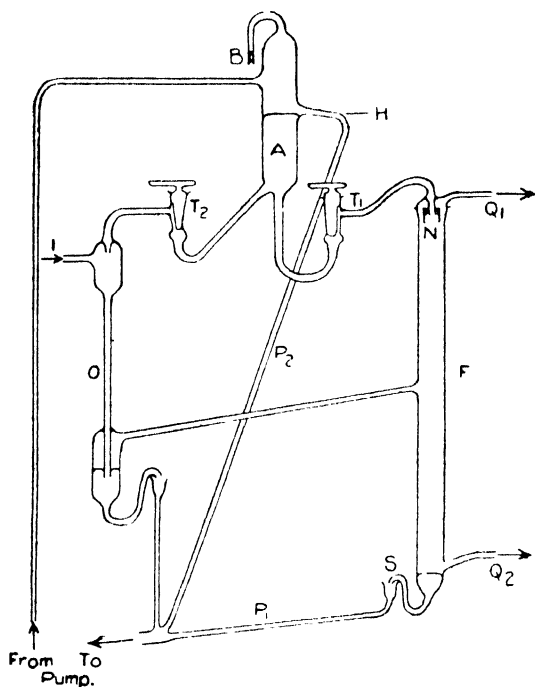


Fig. 89.—Apparatus of Oliphant for Sorption by a Mercury Surface.

was 3, 5, 7, 7, and 8×10^{14} molecules when the carbon dioxide was 0.5, 2, 5, 10 and 50 per cent, respectively, of the hydrogen mixture. The error in the last measurement is magnified and may be 50 per cent. Assuming that carbon dioxide molecules occupy cubes of $4.2 \text{ \AA.}$, 6×10^{14} would form a monomolecular layer.

Most authorities consider that the calculation of the amount of adsorption by means of the Gibbs equation is fully as valid

as an actual measurement.¹ Iredale,² therefore, measured the surface tension by the drop weight method, the drops being formed in the presence of organic vapours in air. At one point the calculated adsorption of methyl acetate was 3.7×10^{14} molecules per square centimetre. Similarly, with benzene the maximum adsorption was approximately monomolecular but decreased considerably as the relative humidity, p/p_s , was further increased. With water vapour, however, there was a steady increase of adsorption with increase of vapour pressure, the calculation yielded only 1.8×10^{-8} grams per square centimetre instead of that expected for a monomolecular film (3×10^{-8}). Surface tension was also deduced from the form of large drops of mercury in the presence of various pressures of organic vapours. From these the calculated adsorption of ethyl alcohol, and especially of propyl chloride and of ethyl bromide, is less than that of a close packed monomolecular layer. Methyl iodide affected the surface tension irreversibly and the calculated area per molecule was 13×10^{-16} sq. cm.

Using a microbalance, Volmer and Mahnert³ showed that the amount of benzophenone which is carried away on the surface of drops of mercury issuing from a platinum capillary in contact with a crystal of benzophenone amounts to about half of that required for a close packed monomolecular layer.

In conclusion, two observations on the wetting of glasses may be mentioned. Mercury ordinarily does not wet glass, owing, presumably, in large measure to the gas sorbed upon

¹ But cf. W. C. McC. Lewis, *Phil. Mag.*, (6), 1908, **15**, 499; 1909, **17**, 466; *Z. physik. Chem.*, 1910, **73**, 129; *Science Progress*, 1916, **11**, 199; J. W. McBain and G. P. Davies, *J. Am. Chem. Soc.*, 1927, **49**, 2230; W. D. Harkins and D. M. Gans, *Colloid Symposium Monograph* (Michigan, 1927), 1928, **5**, 40; (Toronto, 1928), 1928, **6**, 36; M. E. Laing, J. W. McBain and E. W. Harrison, *Colloid Symposium Monograph* (Toronto, 1928), 1928, **6**, 63; J. W. McBain and R. DuBois, *J. Am. Chem. Soc.*, 1929, **51**, 3534.

² T. Iredale, *Phil. Mag.*, (6), 1923, **45**, 1088; 1924, **48**, 177; 1925, **49**, 603.

³ M. Volmer and P. Mahnert, *Z. physik. Chem.*, 1925, **115**, 249.

the glass. Schumacher ¹ showed that after rigorous evacuation for two days at a temperature of at least 400° C., fused silica is wetted at room temperature by mercury, Pyrex occasionally and soda-glass seldom. Part of the effect in the latter case may be due to a film of sodium hydroxide and silica resulting from hydrolysis.

SORPTION BY PLATINUM AND OTHER NOBLE METALS ²

Warburg and Ihmori ³ with their microbalance sensitive to an adsorbed film of water of about 10 Å. thickness could find no indication of a film of water on clean surfaces of platinum although they were easily measurable upon surfaces which had not been wiped clean. Strömberg ⁴ also used a microbalance from which thin strips of platinum and gold were suspended in an atmosphere of unsaturated water vapour. The sorption became constant within a few hours. The thickness of the water film in a saturated atmosphere was estimated to be 380 and 64 Å., respectively, and in a half saturated atmosphere 42 and 9 Å., respectively, the isotherms being S-shaped.

The appearance of Strömberg's bright platinum foil which had previously been evacuated for two hours at a bright red

¹ E. E. Schumacher, *J. Am. Chem. Soc.*, 1923, **45**, 2255. The floating of mercury droplets upon various powders, such as charcoal or sand, has been shown by G. Tammann and H. Diekmann (*Z. anorg. allgem. Chem.*, 1924, **135**, 194) to be due to surface tension which only permits sinking when paths are opened between the particles of powder during the escape of sorbed gas upon heating or evacuation.

² To the following discussion may be added reference to W. G. Palmer (*Proc. Roy. Soc. (London)*, A, 1924, **106**, 55; 1926, **110**, 133; 1927, **115**, 227; 1929, **122**, 487) who discusses coherer action of tungsten, platinum and carbon filaments in the presence of gases, vapours and non-conducting solutions from the standpoint of monomolecular sorption.

³ E. Warburg and T. Ihmori, *Wied. Ann. der Physik*, 1886, **27**, 505; T. Ihmori, *Wied. Ann. der Physik*, 1887, **31**, 1011.

⁴ R. Strömberg, *Kgl. Svenska Vetenskapsakad. Handl.*, (3), 1928, **6**, No. 2, 1.

heat ¹ is shown in fig. 90.² The surface is furrowed, which Strömberg ascribes to twinning of the very visible countless crystallites. He allowed 40 per cent of extra surface for this furrowing upon the assumption that it is wholly superficial.

The appearance of Strömberg's gold foil after burnishing, boiling in 96 per cent alcohol, boiling in concentrated nitric acid and then several changes of distilled water and drying at 150° C., is shown in fig. 91.³ He allowed an increase of 100 per cent for unevennesses.

Strohhäcker ⁴ found by means of a microbalance that the total amount of air sorbed on gold is approximately that required for a monomolecular layer, but it is significant that 30 hours was required to eliminate the gas even in a vacuum of 10^{-5} mm. This is inconceivably low for a kinetic exchange between the gaseous phase and a fully exposed surface.

Platinum surfaces which had been made catalytically active by contact with a mixture of oxygen and hydrogen at 300° C. and then evacuated at 350° C.⁵ were used in Langmuir's ⁶ studies. "When small amounts of oxygen were allowed to come in contact with the platinum surface, the oxygen disappeared almost instantly, until the total amount adsorbed corresponded to a monomolecular or monatomic film, and then no further amount of this gas could be adsorbed, even with a great increase in pressure. No trace of the oxygen could be pumped off by heating the platinum in the best vacuum to 360°.

¹ Compare this chapter, page 264 (Berliner).

² R. Strömberg, *Kgl. Svenska Vetenskapsakad. Handl.*, (3), 1928, 6, No. 2, 90, figs. 17 and 18.

³ R. Strömberg, *Kgl. Svenska Vetenskapsakad. Handl.*, (3), 1928, 6, No. 2, 104, figs. 22 and 23.

⁴ J. Strohhäcker, *Z. Physik*, 1930, 64, 248.

⁵ 4.03 g. of platinum (together with the glass bulb) thereby evolved 18.3 cu. mm. of hydrogen, 5.8 of carbon monoxide, 17.7 of carbon dioxide, 92 of water vapour and 1.2 of gas, probably nitrogen. The volume of the hydrogen and carbon monoxide was about one-tenth of the volume of the platinum.

⁶ I. Langmuir, *J. Am. Chem. Soc.*, 1918, 40, 1361.

" If the platinum in this condition was allowed to come in contact with hydrogen or carbon monoxide at low pressure, the oxygen film was removed and water vapour or carbon dioxide was produced, even at room temperature, and then an additional amount of hydrogen or carbon monoxide was adsorbed sufficient to produce a monomolecular film of these substances. The carbon monoxide film could be very gradually pumped off at a temperature about 300° .¹ No measurable amounts of nitrogen or carbon dioxide were adsorbed by the platinum at any time."²

From a series of observations Langmuir concluded that the maximum sorption obtainable with either carbon monoxide or oxygen (or hydrogen) was equal to a monomolecular layer. The amount of oxygen sorbed was only one-tenth of this at liquid air temperature, increasing steadily with temperature up to 360°C . Both oxygen and carbon monoxide proved capable of reacting with whichever gas was already upon or within the platinum at room temperature.

The chemical nature of the sorption of oxygen by platinum was demonstrated by Döbereiner³ who showed that when platinum black had sorbed oxygen, it dissolved in hydrochloric acid to form platinum chloride.

Platinum black⁴ differs from platinum in having an enormous surface. The classical investigation of this material is that of Mond, Ramsay and Shields⁵ to which reference should be made. It contains nearly 0.5 per cent of water, about one half of which is removable by evacuation at 130°C . Unless removed by reduction, it also contains nearly 100

¹ I. Langmuir (*J. Am. Chem. Soc.*, 1918, **40**, 1399) found that at liquid air temperature the sorption of carbon monoxide was readily reversible; compare Chapter I, pages 9 and 10, Chapter IV, pages 69, 120 and 121 (sorption of oxygen by charcoal at various temperatures).

² I. Langmuir, *Trans. Farad. Soc.*, 1922, **17**, 612.

³ Quoted by M. E. Mitscherlich, *Taylor's Scientific Memoirs*, 1846, **4**, 1 (from *Ann. chim. phys.*, (3), 1843, **7**, 15).

⁴ F. Kirchner (*Ann. der Physik*, (4), 1922, **69**, 59) obtained no X-ray diagram from a deposit on a very thin copper plate, but A. Osawa (*Science Repts. Tôhoku Imp. Univ.*, (1), 1925, **14**, 45) found it to be the same as ordinary platinum, the lattice expanding uniformly upon the sorption of hydrogen, oxygen and carbon monoxide.

⁵ L. Mond, W. Ramsay and J. Shields, *Phil. Trans. Roy. Soc. London*, A, 1895, **186**, 661; 1897, **190**, 129.

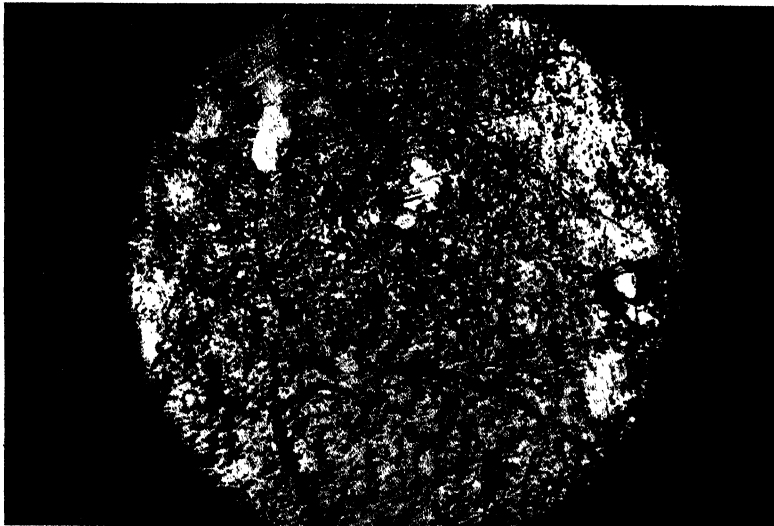
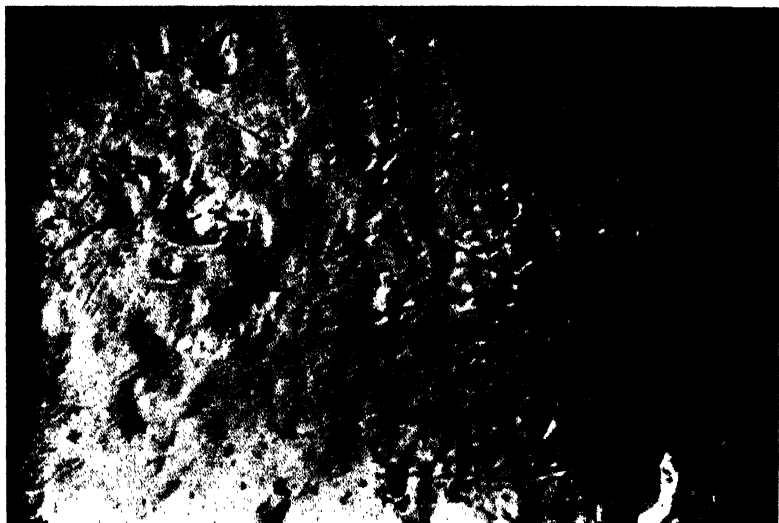


Fig. 91. Appearance of bright gold surfaces magnified 100 (lower) and 1200 (upper) fold in oblique illumination, showing innumerable crystallites and furrows.

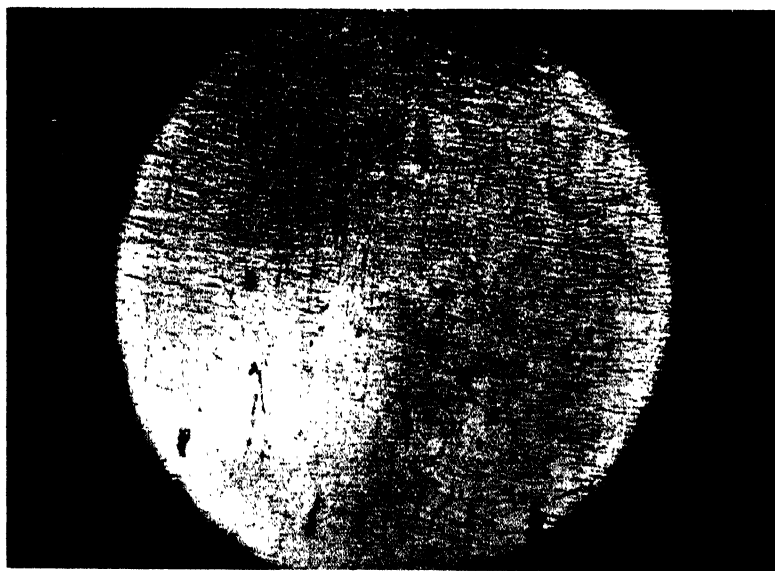
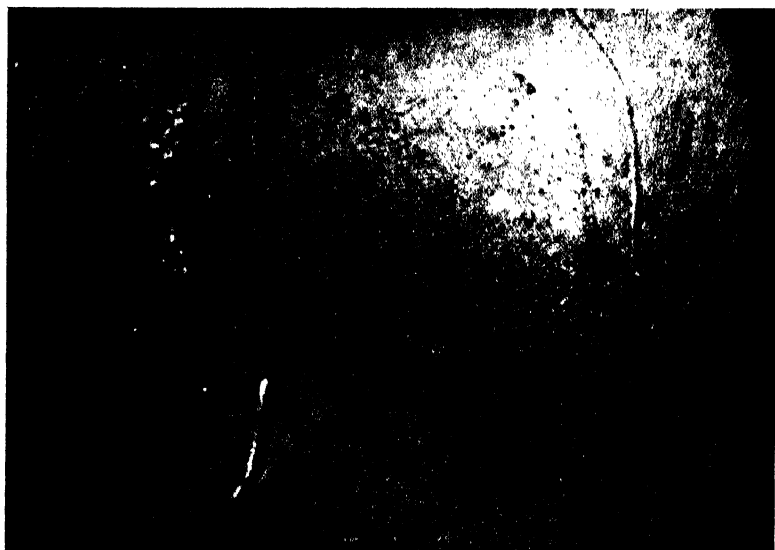


Fig. 90. Appearance of bright platinum surfaces magnified 100 (lower) and 1200 (upper) fold in oblique illumination, showing innumerable crystallites and furrows.

volumes (0.66 per cent by weight) of oxygen and often some carbon dioxide (2.7 to 14.2 volumes). The greater part of the carbon dioxide is removable by evacuation between 100° and 180° C. and the oxygen between 300° and 400° C. In support of the view that sorption of oxygen is superficial oxidation, it is pointed out that the heat of sorption is the same as the heat of formation of platinous hydroxide.

Müller and Schwabe¹ recalculated Mond, Ramsay and Shields' highly curved sorption isotherm for hydrogen, which is nearly constant between 1 and 5 atmospheres, and showed that it agrees excellently with the formula of Zeise,²

$$x/m = \sqrt{\frac{k_1 k_2 p}{1 + k_2 p}}.$$

Platinum black sorbs at room temperature approximately equal volumes of hydrogen, oxygen, carbon monoxide and sulphur dioxide;³ nitrogen and carbon dioxide are sorbed but little. In careful work it is necessary first to remove the film of oxygen, which can only be done by reduction with some such gas as hydrogen.⁴ Taylor and Burns⁵ did this and then attempted to remove the hydrogen by evacuation at 110° in spite of the fact that Mond, Ramsay and Shields had found that nearly 300° was necessary although removal begins at room temperature. Benton⁶ points out that Taylor and Burns had therefore removed not more than half the hydrogen. Carbon monoxide could not be recovered by evacuation.⁵

¹ E. Müller and K. Schwabe, *Z. Elektrochem.*, 1929, **35**, 181.

² H. Zeise, *Z. physik. Chem.*, 1928, **136**, 385.

³ L. Mond, W. Ramsay and J. Shields, *Phil. Trans. Roy. Soc. London*, A, 1895, **186**, 657; 1897, **190**, 129; *Z. physik. Chem.*, 1896, **19**, 25; 1898, **25**, 657; about 100 volumes. See this chapter, page 281, footnote 1.

⁴ A. de Hemptinne (*Z. physik. Chem.*, 1898, **27**, 429; *Bull. sci. acad. roy. Belg.* (3), 1898, **36**, 155) found that platinum black effects the combination of hydrogen and oxygen even at - 190° C.—a remarkable fact, since metallic sodium does not react with sulphuric acid even at - 130° C.

⁵ H. S. Taylor and R. M. Burns, *J. Am. Chem. Soc.*, 1921, **43**, 1273.

⁶ A. F. Benton, *J. Am. Chem. Soc.*, 1926, **48**, 1850.

The best recent study of the sorption of hydrogen, as well as oxygen and carbon dioxide, is that of Benton.¹ The platinum black is evacuated, treated with hydrogen, and subjected to prolonged evacuation at 110° C. To complete the sintering process, the remaining hydrogen was removed by excess of oxygen and the water formed removed by evacuation. Thereupon excess of carbon monoxide is added and the amount of carbon dioxide in the gas recovered at 110° when subtracted from the carbon monoxide which has disappeared measures the carbon monoxide retained; and now by addition of carbon monoxide its total sorption may be studied. Analogous procedures were used for hydrogen and for oxygen.

Benton's isotherm for the sorption of hydrogen at 25° C. is shown in fig. 92.² It will be noted that the results resemble the best obtained for charcoal in that the sorption is practically completed at low pressure and thereafter increases but little. "Hydrogen and carbon monoxide are adsorbed to practically the same extent, while the adsorption of oxygen is somewhat more than half as great."³ "The isotherm for carbon monoxide is even flatter than that for hydrogen. The adsorption

¹ A. F. Benton, *J. Am. Chem. Soc.*, 1926, **48**, 1850; he throws doubt upon the experiments of F. H. Pollard (*J. Phys. Chem.*, 1923, **27**, 356); likewise he suggests that the results of M. C. Boswell and R. R. McLaughlin (*Trans. Roy. Soc. Can.*, (3), 1923, **17**, Sec. III, p. 1) on the adsorption of hydrogen and oxygen on platinum black are vitiated by the unsuspected escape of hydrogen through numerous rubber connexions. Benton deduces from two experiments on carbon dioxide in the presence of hydrogen that these two gases seem to unite to form a very stable complex upon the surface, most of which is not removed by evacuation at 110° C.

² A. F. Benton, *J. Am. Chem. Soc.*, 1926, **48**, 1858, fig. 3. Compare the similar initial portions of hydrogen isotherms found by E. B. Maxted (*J. Chem. Soc.*, 1930, 2099) who noted that the sorptive capacity of the platinum black diminished by one-third in three months. Ninety-four per cent of the total sorption occurred during the first three minutes.

³ On the other hand, G. B. Taylor, G. B. Kistiakowsky and J. H. Perry (*J. Phys. Chem.*, 1930, **34**, 799) found that the ratio of the sorption of oxygen to that of hydrogen varied widely with different preparations of platinum black.

of oxygen appears to be completely irreversible, since none was removed by evacuation, either at 25° or at 110° ."

One volume of Benton's platinum black sorbed at 25° C. and one atmosphere, 36.7 volumes of hydrogen,¹ 37.8 of carbon

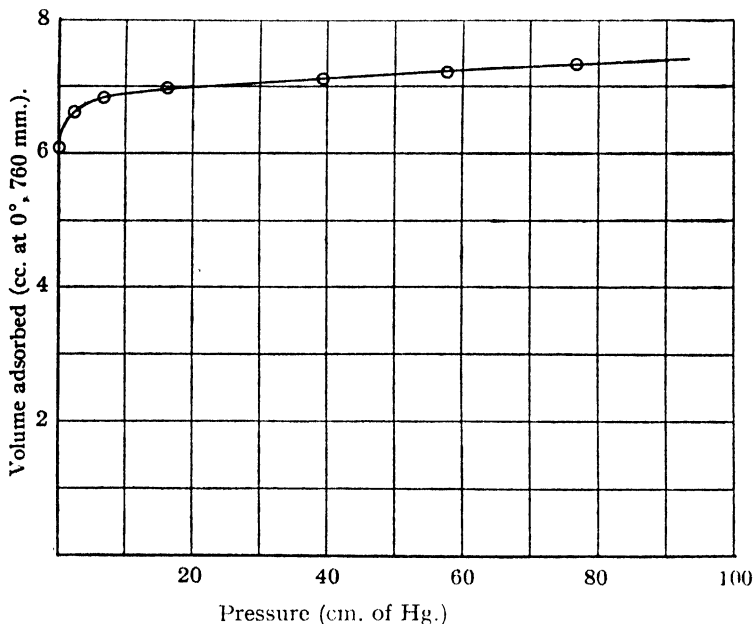


Fig. 92.—Sorption Isotherm for Hydrogen by 4.269 g. of Platinum Black at 25° C.

¹ A. Gutbier and O. Maisch found that their platinum black sorbed as much as 160 volumes of hydrogen, whereas platinum sponge sorbed not more than one volume (*Ber.*, 1919, **52B**, 1368); T. Graham obtained 2.19 with platinum tubing (*Liebig's Ann. Chem. Suppl.*, 1868, **6**, 284); A. Thiel and W. Hammerschmidt, 35 volumes with platinum cathode (*Z. anorg. allgem. Chem.*, 1924, **132**, 15); A. Sieverts and E. Jurisch, none (*Ber.*, 1921, **45**, 221); A. Berliner, 204 to 271 with platinum foil (*Wied. Ann. der Physik*, 1888, **35**, 807; *Jahresbericht über die Fortschritte der Chemie*, 1888, p. 45); L. Mond, W. Ramsay and J. Shields, 0.7 to 3.1 with platinum sponge and 110 to 119 with platinum black (*Z. physik. Chem.*, 1896, **19**, 25; *Phil. Trans. Roy. Soc. London*, A, 1895, **186**, 657; similarly they found 0.5 to 2.4 volumes

monoxide or 20.4 of oxygen. Benton concludes that at higher temperatures the sorption of carbon monoxide and hydrogen would remain unchanged but that the values for oxygen would be more nearly equal to them. From this independence of temperature and pressure Benton infers that the sorption is due to a monomolecular layer and that therefore his platinum black had a surface area of 1.3×10^6 sq. cm. per cubic centimetre, or 6.0 square metres per gram, or less than one per cent of that attributed to active charcoal.

Boswell and McLaughlin,¹ reviewing their experiments on hydrogen, oxygen and their mixtures with nitrogen, concluded that a surface film of hydrogen, or of mixed hydrogen and oxygen, may be independent of any underlying internal content of oxygen at temperatures up to 150° C. The adsorbed hydrogen upon the surface consists of positively and negatively charged hydrogen atoms. The mixed film is thought to consist of the ions of water. The suggestion of definite hydrides or peroxide hydrides of platinum is rejected.

The well known incandescence of platinum black when in contact with a mixture of air and the vapour of alcohol is due, not to the heat of sorption, but to the heat of oxidation of alcohol upon the surface.² The heat of sorption is so small that the reaction could not be initiated thereby in the gaseous phase.

Sulphur dioxide is sorbed irreversibly by platinum black.³ One volume of the black at 25° C. sorbed 84 volumes (at N.T.P.) of which only 30 volumes could be desorbed after of oxygen with platinum sponge); G. Neumann and F. Streintz, 49.3 with platinum black (*Monatsh.*, 1891, **12**, 653); Berthelot, 82 to 123 fold with platinum black (*Bull. soc. chim.*, 1883, **39**, 109); H. S. Taylor and R. M. Burns, 6.85 with platinum black (*J. Am. Chem. Soc.*, 1921, **43**, 1273); F. H. Pollard, 200 volumes using platinized asbestos (*J. Phys. Chem.*, 1923, **27**, 356); C. Paal and C. Auerswald, 747 in colloidal solution (*Ber.*, 1927, **60B**, 1648); E. Müller and K. Schwabe, 500 to 1070 with very finely divided platinum (see this chapter, pages 293 and 294).

¹ M. C. Boswell and R. R. McLaughlin, *Trans. Roy. Soc. Can.*, (3), 1923, **17**, Sec. III, p. 1.

² L. B. Loeb, *Proc. Nat. Acad. Sci.*, 1920, **6**, 107.

³ D. O. Shiels, *J. Phys. Chem.*, 1929, **33**, 1175.

8½ hours heating at 250° C. The black was subsequently found to contain sulphur trioxide. However, in similar experiments with asbestos and platinized asbestos sorption of sulphur dioxide was reversible.¹

Even helium is appreciably sorbed.² By means of an electrical discharge in a small tube, platinum was deposited in an atmosphere of spectroscopically pure helium. Upon examination of the deposit so obtained, it was found that the sorption of helium, amounting to 14–34 c.c. per gram of platinum deposited, began with the appearance of the deposit of platinum. The deposit of helium and platinum can be decomposed in a vacuum at temperatures between 90° C. and 160° C. When thus thermally decomposed, the relation between the volume of helium evolved and the temperature resembles the decomposition relations of heterogeneous systems. An examination by ultraviolet photomicrography indicated structural differences between the platinum-helium deposit and the platinum obtained after thermal decomposition. In explanation of the observations, it is proposed that the helium is held in some state of combination with a part of the platinum.

Helium is not sorbed at all by palladium nor does it dissolve therein even in traces.³ Palladium is completely impermeable to helium even at a red heat.

Gutbier and Schieferdecker⁴ studied the sorption of hydro-

¹ D. O. Shiels, *J. Phys. Chem.*, 1929, **33**, 1167.

² H. Damianovich, *Anales soc. españ. fís. quim.*, 1928, **26**, 365; through *Chemical Abstracts*, 1929, **23**, 1537.

³ F. Paneth and K. Peters, *Z. physik. Chem.*, Abt. B., 1928, **1**, 262.

⁴ A. Gutbier and W. Schieferdecker, *Z. anorg. allgem. Chem.*, 1929, **184**, 316; superseding or correcting previous publications and referring to dissertations: see A. Gutbier, H. Gebhardt and B. Ottenstein, *Ber.*, 1913, **46**, 1453; A. Gutbier, B. Ottenstein and G. L. Weise, *Ber.*, 1919, **52B**, 1366, 2275. In the earlier papers it had been overlooked that carbon dioxide and hydrogen interact in or upon the platinum metals to form a certain amount of carbon monoxide and water even at low temperature. F. Graf (*Dissert.*, Jena, 1926, pp. 17 and 36) has observed the sorption of carbon monoxide, hydrogen and nitrogen by iridium at various temperatures and also the mixture of gases evolved upon heating ruthenium black which had been exposed to carbon dioxide.

gen by iridium, iridium black, ruthenium black and osmium black and of carbon monoxide by iridium black. Grey iridium powder, previously exposed to hydrogen, was evacuated at 350°C . yielding 0.1 c.c. of gas. After that, sorbed hydrogen could be quantitatively recovered by evacuation at 400°C . 1.054 g. of iridium sorbed the following volumes (presumably measured at room temperature and pressure) :

$^{\circ}\text{C}$.	22	110	150	180	130	86	47	22	55	70
c.c. sorbed	1.09	0.77	0.65	0.69	0.76	0.90	1.06	1.15	0.89	0.99

On evacuation at 600°C ., 0.29 c.c. extra was recovered and the metal was sintered. Thereafter the sorption at 22° had fallen to 0.29 and 0.23 c.c. It seems evident that Benton's criticism of earlier work by Gutbier's collaborators and others applies also here ; namely, that the different points on the isobar do not refer to specimens whose previous heat treatment was the same. Upon repeating this experiment with a larger amount of iridium, the sorption per gram was less than half as great, showing the lack of uniformity in the powder. The authors state that they are unable to remove any of the hydrogen by evacuation below 50°C .

Iridium in the form of black, previously dried, and evacuated at 350°C ., reacted at room temperature with hydrogen so violently that it was thrown out of the container, water being formed. 0.446 grams of black thus used 5.5 c.c. of hydrogen. Hydrogen cannot be completely recovered from the black without destroying the latter by heating to redness in vacuo. One gram of black sorbed between 5.9 and 3.2 c.c. at various temperatures between 17°C . and 190°C ., or 140 volumes at 20°C .,¹ the amounts being greatest for the lower temperatures. At 600°C . the material was sintered and grey. Between 4 and 9 c.c. of carbon monoxide were taken up per gram. It is retained most tenaciously.

¹ I. I. Zhukov found 807 volumes at 25° (*Ann. inst. anal. phys. chim.* (Leningrad), 1927, **3**, 600 ; through *Chemical Abstracts*, 1928, **22**, 4399) ; F. Rother found after long cathodic bombardment in vacuo about 800 volumes at room temperature (*Ber. K. Sächs. Ges. Wiss. Math.-Phys. Kl.*, 1912, **64**, 5) ; see the measurements of Müller and Schwabe, this chapter, pages 293 and 294.

Ruthenium black ¹ took up about two and one-half times as much hydrogen and the osmium black ¹ nearly five times as much as the iridium black. Müller and Schwabe ² found that the very large amount of hydrogen sorbed by their osmium black was mostly displaced by wetting with water. The hydrogen could be recovered quantitatively only at high temperatures (above 650° C.).

Rhodium black at 20° sorbed 114 volumes of hydrogen and at 0°, 206 volumes. Zhukov ³ found 448 volumes at 25°, whereas between 420° and 1,020° C. Sieverts and Jurisch ⁴ found it negligible.

In a detailed study of "clean-up" by a molybdenum filament, Langmuir ⁵ has adduced the following facts. The possibility that a molybdenum filament heated in a fairly high vacuum (0.03 mm. and less) to a temperature at which vaporization occurs (2,000°–2,400° K.) may clean up nitrogen more efficiently than tungsten, since it evaporates more rapidly, is not realized experimentally. The rate of evaporation was found to be the same as in vacuum; hence nitrogen does not attack the molybdenum filaments.⁶ Denoting by ϵ the ratio of the number of molecules of nitrogen cleaned up to the number of atoms of molybdenum evaporating in the same time, the following experimental facts are outstanding: ϵ is always less than 1, is independent of pressure and decreases as the bulb and filament temperature is raised. The highest values were about 0.4 and the lowest 0.01. There is no clean-up in the presence of any water vapour, as is true when carbon

¹ Compare the systematic measurements of Müller and Schwabe, this chapter, pages 293 and 294.

² E. Müller and K. Schwabe, *Z. Elektrochem.*, 1929, **35**, 184.

³ I. I. Zhukov, *Ann. inst. anal. phys. chim.* (Leningrad), 1927, **3**, 600; through *Chemical Abstracts*, 1928, **22**, 4399.

⁴ A. Sieverts and E. Jurisch, *Ber.*, 1912, **45**, 221.

⁵ I. Langmuir, *J. Am. Chem. Soc.*, 1919, **41**, 167.

⁶ J. H. de Boer (*Proc. Acad. Sci. Amsterdam*, 1928, **31**, 906) points out that salts are commonly introduced into electric lamps to decolorize metal evaporated from the filament, either through combination (as with chlorine liberated by K_2TiCl_6) or by sorption (as with NaCl or CaF_2 which yield large surfaces upon evaporation onto glass).

monoxide is used instead of nitrogen, and ϵ is unity. The author presents a theory of the mechanism of the clean-up from the observed facts to the effect that molybdenum atoms and nitrogen molecules combine to form at least two products; namely, the very stable NMoN from the colliding molecules of low relative translational velocity and high rotational velocity of the nitrogen molecules, and the secondary compound Mo : N₂. The latter decomposes on striking the bulb on account of the greater attraction of the molybdenum atoms for each other. This theory is used to account for the nature of the metallic deposit, its spongy character, the loss of only part of the nitrogen from it, which cannot be entirely re-absorbed by it, the absorption of nitrogen but not of hydrogen when the sponge is cooled with liquid air, complete chemical combination with nitrogen at 270° and extreme activity such that water is decomposed at room temperature.

SORPTION OF HYDROGEN BY PALLADIUM

Upon the basis of thirty-eight references and much other material Smith¹ reviews the occlusion of hydrogen by metallic elements and distinguishes "hydrogen alloys" (occlusion) from hydrogen compounds such as the non-metallic volatile type, SbH₃, and the crystalline transparent type, CaH₂. The metals which occlude hydrogen all seem to be within the central group of Werner's periodic table as shown in fig. 93.² The right half of the table has been placed above the left half from considerations of space. The reader may wish to alter the print used for several of the elements such as iridium, ruthenium and osmium. The behaviour of the elements in the upper right hand and lower left hand corners of the table is so familiar that Smith has not described it in the table.

Of the forty-nine elements of this group, thirteen are uninvestigated with regard to occlusion; of the remaining thirty-six, more than half occlude hydrogen to a measurable extent. With few exceptions power of occlusion appears to go with

¹ D. P. Smith, *J. Phys. Chem.*, 1919, **23**, 186.

² D. P. Smith, *J. Phys. Chem.*, 1919, **23**, 189; compare A. Sieverts, *Z. Metallkunde*, 1929, **21**, 39.

high values of specific magnetic susceptibility; that is, of strongly magnetic character.

The interaction of hydrogen and palladium has received an exceptional amount of attention ever since Graham's discovery that even in massive form such as foil or wire, this metal takes up enormous quantities of hydrogen which permeates the whole mass. All the older authorities considered that hydrogen was here in the metallic form which they called hydrogenium, the latter being alloyed with the palladium in analogy with ammonium amalgam. Much effort was spent in attempts to deduce the properties of hydrogenium from the difference in physical properties with and without hydrogen. Dewar¹ pointed out that the amount of hydrogen never exceeded the proportions Pd_3H_2 , but no one has yet employed really high pressures. The most plausible modern interpretation is that at least half of the palladium atoms in the space lattice may be replaced by the compound PdH .

The measurements of the sorptive capacity of palladium² in its various forms may be summarized as follows.

Graham³ found that one volume of palladium foil sorbs 330 volumes of hydrogen; one volume of palladium wire charged with hydrogen by using it as cathode took up 867 to

¹ J. Dewar, *Trans. Roy. Soc. Edin.*, 1876, **27**, 169.

² A. Sieverts (*Z. anorg. allgem. Chem.*, 1915, **92**, 329) has shown that palladium is surpassed at slightly elevated temperatures by an alloy of palladium containing 40 per cent silver. Other alloys of palladium likewise strongly sorb hydrogen, for example, palladium with platinum, gold or silver (T. Graham, *Proc. Roy. Soc. (London)*, 1869, **17**, 212, 500; *J. Chem. Soc.*, 1869, **22**, 419; *Pogg. Ann. der Physik*, 1869, **136**, 317; 1869, **138**, 49; *Compt. rend.*, 1869, **68**, 101, 1511; *Chem. News*, 1869, **19**, 52; 1869, **20**, 16). F. Krüger and A. Sacklowski (*Ann. der Physik*, (4), 1925, **78**, 76) with cathodically charged alloy obtained linear decrease with increase of silver until no hydrogen was sorbed when the alloy contained 70–80 per cent of silver. A. J. Berry (*J. Chem. Soc.*, 1911, **99**, 465) obtained an identical result with alloys of palladium and gold.

³ T. Graham, *J. Chem. Soc.*, 1867, **20**, 235; *Liebig's Ann. Chem. Suppl.*, 1868, **6**, 284; *Phil. Mag.*, (4), 1866, **32**, 401; *Proc. Roy. Soc. (London)*, 1868, **16**, 422; 1869, **17**, 212, 500; *Pogg. Ann. der Physik*, 1866, **129**, 549; 1869, **136**, 317; 1869, **138**, 49.

982 volumes. Lisenko ¹ attained by this method 854 to 856 volumes. Berliner ² found 800 to 860 volumes with palladium foil but only when its surface had been cleaned by using it as anode in dilute sulphuric acid. Holt, Edgar and Firth ³ with a fresh specimen of palladium foil which took up no hydrogen at all were able to "activate" it by heating in the air followed by reduction or by heating in a vacuum or in an atmosphere of hydrogen so that it took up 712 to 869 volumes. Sieverts ⁴ found 650 volumes, and Baerwald ⁵ 920 volumes at 20° as well as at — 185° C.

In the form of sponge palladium takes up 655,⁶ 782,⁷ 852,⁸ or 661 volumes ⁹ of hydrogen.

Palladium in the form of black took up 725,¹⁰ 873,¹¹ 771,¹² or 734 ¹³ volumes of hydrogen; or, in the dry condition, 392 ¹⁴ to 674 ¹⁴ volumes, but under water, 1,204 ¹⁵ volumes. Firth ¹⁶

¹ Lisenko, *Ber.*, 1872, **5**, 29.

² A. Berliner, *Wied. Ann. der Physik*, 1888, **35**, 791; *Jahresber. Fortschritte Chem.*, 1888, p. 42.

³ A. Holt, E. C. Edgar and J. B. Firth, *Z. physik. Chem.*, 1913, **82**, 513.

⁴ A. Sieverts, *Z. physik. Chem.*, 1914, **88**, 121; interpolated by Müller and Schwabe for the values at 0° and 80° C.

⁵ H. Baerwald, *Ann. der Physik* (4), 1907, **23**, 105.

⁶ T. Graham, *J. Chem. Soc.*, 1867, **20**, 235; *Liebig's Ann. Chem. Suppl.*, 1868, **6**, 284.

⁷ Trommsdorf; quoted by C. Hoitsema, *Z. physik. Chem.*, 1895, **17**, 1.

⁸ L. Mond, W. Ramsay and J. Shields, *Phil. Trans. Roy. Soc. London*, A, 1898, **191**, 105; the same sponge sorbed only two volumes of sulphur dioxide or 17 volumes of carbon monoxide.

⁹ A. Gutbier, H. Gebhardt and B. Ottenstein, *Ber.*, 1913, **46**, 1453.

¹⁰ C. Hoitsema, *Z. physik. Chem.*, 1895, **17**, 1.

¹¹ L. Mond, W. Ramsay and J. Shields, *Phil. Trans. Roy. Soc. London*, A, 1898, **191**, 105; the same black sorbed only 90 volumes of sulphur dioxide.

¹² A. Sieverts, *Z. physik. Chem.*, 1914, **88**, 103.

¹³ I. I. Zhukov, *Ann. inst. anal. phys. chim.* (Leningrad), 1927, **3**, 600; through *Chemical Abstracts*, 1928, **22**, 4399.

¹⁴ C. Paal and C. Amberger, *Ber.*, 1905, **38**, 1397.

¹⁵ C. Paal and J. Gerum, *Ber.*, 1908, **41**, 818.

¹⁶ J. B. Firth, *J. Chem. Soc.*, 1920, **117**, 171; 1921, **119**, 1120.

found 778 to 817 volumes, later, like others, showing that it depended upon the method of preparation and also upon whether the palladium had been cooled from 100°C . in the atmosphere of hydrogen or in vacuum with subsequent exposure to hydrogen. Thus with the two procedures, palladium obtained by reducing palladium chloride in hydrogen at 100°C . took up 796 to 702 volumes; prepared with hydrazine, 801 and 736 volumes; prepared with formate, 879 and 849. Finally, if the black was prepared from the oxide with hydrogen, it took up 852 and 804 volumes, respectively.

Firth¹ showed that the amount of hydrogen sorbed by palladium black was 25 to 30 per cent greater at -190°C . than at 20°C .² It may then increase again up to 100°C .³ Sieverts⁴ showed that the amount sorbed by wire at 140°C . and one atmosphere pressure fell to about one-half on heating from 140° to 200° and to one-fourth at 400° but only to about one-fifth at higher temperatures up to the melting-point ($1,550^{\circ}\text{C}$.), whereupon it was reduced to about one-twelfth; the values for black, originally higher, approached those for wire between 500° and 600° . Black becomes sponge between 400° and 600°C . Dewar⁵ showed that a rod of palladium at 500°C . may sorb 300 volumes of hydrogen under 100 to 120 atmospheres.

It will be noted that irrespective of the form of the palladium, whether foil, sponge or black, it takes up 650 to 900 volumes of hydrogen, black being better than sponge or foil, although sometimes the latter is quite inactive. Hence absorption or

¹ J. B. Firth, *J. Chem. Soc.*, 1921, **119**, 1120; but compare H. Baerwald, *Ann. der Physik* (4), 1907, **23**, 105.

² A. de Hemptinne (*Bull. sci. acad. roy. Belg.* (3), 1898, **36**, 155; *Z. physik. Chem.*, 1898, **27**, 429) made the unexplained observation that if palladium containing carbon monoxide is gradually warmed in an atmosphere of hydrogen from -78°C ., sorption suddenly sets in at 20°C .

³ J. B. Firth, *J. Chem. Soc.*, 1921, **119**, 1120; but compare H. Baerwald, *Ann. der Physik* (4), 1907, **23**, 105; A. Gutbier, H. Gebhardt and B. Ottenstein, *Ber.*, 1913, **46**, 1453.

⁴ A. Sieverts, *Z. physik. Chem.*, 1914, **88**, 103.

⁵ J. Dewar, *Proc. Chem. Soc.*, 1897, **13**, No. 183, p. 192.

solid solution is recognized by Sieverts as of major importance at room temperature.

Inactive massive palladium has been observed by a number of authors. Thus Mond, Ramsay and Shields ¹ state that new palladium foil

"scarcely occluded any hydrogen even after ignition in the gas and subsequently cooling down. It was therefore charged and discharged several times electrolytically with hydrogen, but still it persistently refused to occlude any appreciable quantity when replaced in an atmosphere of hydrogen.

"After powerful ignition in the blowpipe flame, when it was probably oxidized and then again reduced at a still higher temperature, it was introduced once more into the experimental tube. It immediately occluded a considerable quantity of hydrogen, and by maintaining the temperature between 100° and 130°, a large additional quantity was slowly absorbed. On cooling down to the ordinary temperature, hydrogen was again occluded, and it was finally found to have taken up 846 volumes."

Compact palladium can sorb but very little hydrogen unless charged electrolytically, or expanded by heat treatment or progressive action of oxygen or hydrogen.

Tammann and Schneider ² found that hard palladium foil does not sorb appreciable amounts of gaseous hydrogen in half an hour between 100° and 200° C., unless it has first been heated at 400° C., whereupon it sorbs hydrogen at 150° C. at the greatest velocity. Heating to still higher temperatures progressively diminished the velocity at 150° C. so that 400° C. was the optimum temperature of activation. The original hard palladium foil used as cathode in electrolysis took up hydrogen with almost the same velocity as after any other treatment. Nickel and iron show an almost opposite behaviour. Heating palladium foil to 350° did not alter its structure, but at 450° a new, very fine grain appeared and the new crystallites grew rapidly coarser on heating to higher

¹ L. Mond, W. Ramsay and J. Shields, *Phil. Trans. Roy. Soc. London*, A, 1898, **191**, 105.

² G. Tammann and J. Schneider, *Z. anorg. allgem. Chem.*, 1928, **172**, 43.

temperatures. Repeated sorption of hydrogen ¹ may render palladium foil "much crumpled and rather friable". A "wire becomes fissured longitudinally, acquires a thready structure, and is much disintegrated".¹ The effect of heating with hydrogen was held to invalidate Halla's suggestion ² that inactivation of palladium, which sometimes occurs, is due to a superficial film of oxygen. However, Tammann and Schneider ³ showed that exposure of palladium foil (not black) could greatly retard the sorption of hydrogen, either from a gas or during electrolysis, unless the palladium was subsequently heated. Since hydrogen combines with oxygen through contact with palladium foil at room temperature, this protective action is ascribed by Tammann and Schneider to stoppage of the openings of the space lattice with water molecules. In proof thereof they showed that the effect did not occur if no hydrogen were present in the palladium before exposure to the air. Palladium foil after heating to 400° C. has sorptive values which are rendered independent of its previous history.⁴

Paal and Gerum ⁵ found that palladium in colloid solution took up 926 to 2,952 volumes of hydrogen; although, as

¹ T. Graham, *J. Chem. Soc.*, 1869, **22**, 423; *Proc. Roy. Soc. (London)*, 1869, **17**, 212, 500; *Chemical and Physical Researches*, 1876, p. 267.

² F. Halla, *Z. physik. Chem.*, 1914, **86**, 496; compare T. Graham, *Chem. Zentr.*, 1867, **38**, 135.

³ G. Tammann and J. Schneider, *Z. anorg. allgem. Chem.*, 1928, **172**, 56.

⁴ For cathodic sorption of oxygen and hydrogen by palladium electrodes see T. Graham, *Chemical and Physical Researches*, 1876, p. 284; J. Dewar, *Chem. News*, 1897, **76**, 274; M. Thoma, *Z. physik. Chem.*, 1889, **3**, 69; F. Fischer, *Ann. der Physik* (4), 1906, **20**, 503; *Dissert.*, Leipzig, 1906; E. A. Harding and D. P. Smith, *J. Am. Chem. Soc.*, 1918, **40**, 1508; 1919, **41**, 1892, 1897; E. Newbery, *J. Am. Chem. Soc.*, 1919, **41**, 1887, 1895; A. Coehn and H. Baumgarten, *Z. physik. Chem.*, 1927, **130**, 545; E. Bülmann and A. Klit, *Z. physik. Chem.*, 1927, **130**, 506; G. Wolf, *Z. physik. Chem.*, 1914, **87**, 575; G. Tammann and J. Schneider, *Z. anorg. allgem. Chem.*, 1928, **172**, 43. For activation, giving platinum, palladium and silver a porous structure reminiscent of charcoal, through suitable heat treatment *in vacuo*, see Miss M. A. Schirmann, *Z. tech. Physik*, 1929, **10**, 637. Most of the foregoing references are discussed in Chapter XIII.

⁵ C. Paal and J. Gerum, *Ber.*, 1908, **41**, 818.

Müller and Schwabe points out, an unknown part of this might be due to oxygen in or upon the palladium, whereas they themselves had ascribed it to variations in the surface.

Sabalitschka ¹ studied palladium precipitated as hydroxide upon various carriers and reduced in a current of hydrogen, giving 2.5 per cent by weight of palladium. The material was dried and evacuated at 300° C. The sorptive capacity first rises and then falls by repeated evacuation at 300° and charging with hydrogen at room temperature, which Sabalitschka ascribes to transition of an amorphous to a crystalline form of palladium. One volume of palladium spread out on sponge char, barium sulphate, blood charcoal, bone charcoal, kieselguhr, and beech charcoal took up 4,581, 3,895, 2,924, 2,167, 910, and 867 volumes of hydrogen, respectively. Repeated treatments finally reduced these values to those for palladium foil.

The comparative independence of the state of subdivision distinguishes palladium from the other platinum metals in its behaviour towards hydrogen. They may also be made to take up enormous amounts of hydrogen but only in very finely subdivided condition, as, for example, when reduced by hydrogen from the oxide. Measurements of this sort have been made by Müller and Schwabe ² who took the greatest care in the purification of all materials used. Of their seventy-nine experiments the following may be selected for quotation, and the isobars in fig. 94 ³ may be reproduced here for comparison with the series of other metallic elements. Thus one volume of titanium sorbs 1,800 volumes and one volume of thorium 1,700 volumes of hydrogen.

¹ T. Sabalitschka, *Arch. Pharm.*, 1927, **265**, 416; T. Sabalitschka and W. Moses, *Ber.*, 1927, **60B**, 786.

² E. Müller and K. Schwabe, *Z. Elektrochem.*, 1929, **35**, 165.

³ A. Sieverts, *Z. Metallkunde*, 1929, **21**, 41, fig. 8; from A. Sieverts and G. Müller-Goldegg, *Z. anorg. allgem. Chem.*, 1923, **131**, 65 (Ce and La); A. Sieverts and E. Roell, *Z. anorg. allgem. Chem.*, 1925, **146**, 149 (Ce and La); 1926, **150**, 261 (Pr and Nd); 1926, **153**, 289 (Zr and Th); H. Huber, L. Kirschfeld and A. Sieverts, *Ber.*, 1926, **59B**, 2891 (V and Ti); A. Sieverts and E. Bergner, *Ber.*, 1911, **44**, 2394 (Ta).

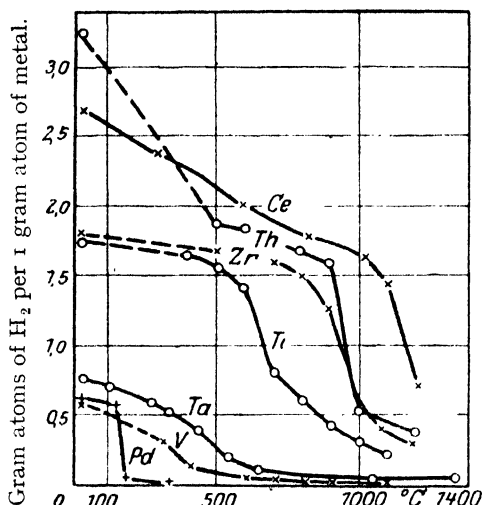


Fig. 94.—Isobars for one Atmosphere of Hydrogen, showing the number of Gram Atoms of Hydrogen sorbed by one Gram Atom of Different Metals at Various Temperatures.

TABLE 40

Volumes of Hydrogen Sorbed by One Volume of Metal at 18° C. and One Atmosphere Pressure

Temp. of Reduction	Pd	Pt *	Ir	Ru	Rh	Os
20°	880	760	1,100	1,520	1,240	1,660
	910	460	—	1,520	1,170	1,620
20°, then 2 hours at	1,030	1,070	850	860	770	980
60° {	850	—	—	1,050	1,030	—
	930	860	790	650	580	1,030
20°, then 75° . {	990	890	670	670	560	890
	780	780	660	550	560	910
	800	900	—	640	480	920
50°, then 70° . {	730	560	540	390	140	690
	740	500	—	470	160	660
60°, then 90–100° {	—	—	160	200	—	—
	—	—	—	84	—	—

* Platinum derived by the reduction of platinous chloride sorbed only about 200 volumes of hydrogen.

The amounts sorbed depend upon temperature and duration of the process of reduction, the method of preparing the oxide, and the rate at which the oxygen is introduced. At the

moment of formation these metals take up more hydrogen than they do when subsequently exposed to hydrogen. They may even take up some hydrogen which they soon relinquish. For example, with palladium a maximum amount was sorbed at two hours. Some was then expelled until after 8 hours constant value was attained. The amount rejected was about 10 per cent. This was ascribed to change in aggregation and therefore in surface. Presence of hydrogen helps all but palladium to maintain their original dispersion.

The preponderating effect of subdivision points to adsorption as the principal factor except in the case of palladium.¹ Hydrogen adsorbed on these metals is probably in atomic form. Hydrogen atoms can usually penetrate freely the space lattice or at least the intergranular spaces of palladium. It may therefore facilitate the aggregation of palladium as distinguished from the other platinum metals. The use of a mechanical framework, as in the case of platinized asbestos, helps to maintain high dispersion and large area. The hardness of crystals goes parallel with closeness of space lattice. The hardness of palladium is 4.0. The others vary from 4.3 for platinum to 6.0, 6.5, 7.0 and 7.5 for rhodium, iridium, osmium and ruthenium, respectively. Sieverts² is of the opinion that hydrogen cannot penetrate any compact metal with hardness greater than 4.

The isotherms for the sorption of hydrogen by palladium exhibit an extraordinary form, not agreeing exactly with any simple interpretation and not definitely explained in spite of numerous careful investigations.

The isotherms with foil, sponge or black differ in detail according to previous history and the exact procedure of the experiment, but they all agree in consisting each of three portions, an initial portion where sorption and pressure both change rapidly, then an intermediate portion almost but not quite parallel with the composition axis where large amounts

¹ A. Coehn (*Z. Elektrochem.*, 1929, **35**, 678) shows that hydrogen may migrate long distances through palladium wire in the form of protons.

² A. Sieverts and A. Gotta, *Z. anorg. allgem. Chem.*, 1928, **172**, 1.

of hydrogen are sorbed with but slight increase of pressure, followed by a final rapid rise in pressure upon further small increments of sorption.

This is illustrated by the experimental diagram of Hoitsema and Roozeboom, fig. 95.¹ The diagram strikingly resembles that for a pair of solid solutions partially immiscible but becoming more nearly miscible as the temperature is raised. However, if this were the whole explanation, the middle portion should be accurately horizontal in agreement with the phase rule, and its junctions with the initial and final portions of the isotherm should be sharp breaks instead of being rounded off. Finally, to some authors it has seemed more than a coincidence that the final steep rise sets in when the solid has approximately the composition of the plausible compound Pd_2H (or Pd_3H_2).² Troost and Hautefeuille³ had assumed that the first part represented solution of hydrogen in palladium, then came formation of Pd_2H at an approximate dissociation pressure, and finally solution of hydrogen in Pd_2H . Hoitsema emphasized the inconclusiveness of the assumption that Pd_2H (or Pd_3H_2) exists. The constancy of the heat of sorption over the whole range of sorption⁴ is also opposed to the view that such a compound is formed.

Holt, Edgar and Firth⁵ sought to explain the phenomena

¹ C. Hoitsema, *Z. physik. Chem.*, 1895, **17**, 19, fig. 7. Compare, for example, A. Gutbier and W. Schieferdecker, *Z. anorg. allgem. Chem.*, 1929, **184**, 315.

² L. Mond, W. Ramsay and J. Shields, *Phil. Trans. Roy. Soc. London*, A, 1898, **191**, 105. Palladium black, dried at 100°C ., contains 138 volumes of oxygen and 0.72 per cent by weight of water. Oxygen cannot be removed by evacuation at a red heat, and the amount taken up at that temperature greatly exceeds that required to form Pd_2O and would probably attain PdO in time. It is thus much more readily oxidized than platinum.

³ L. Troost and P. Hautefeuille, *Compt. rend.*, 1874, **78**, 686; *Ann. chim. phys.* (5), 1874, **2**, 279; *Pogg. Ann. der Physik*, 1874, **153**, 144.

⁴ P. A. Favre, *Ann. chim. phys.* (5), 1874, **1**, 209; L. Mond, W. Ramsay and J. Shields, *Phil. Trans. Roy. Soc. London*, A, 1898, **191**, 105.

⁵ A. Holt, E. C. Edgar and J. B. Firth, *Z. physik. Chem.*, 1913, **82**, 513.

on the basis of quick reversible adsorption and a slower solution or absorption. Firth¹ summarized his conclusions thus:

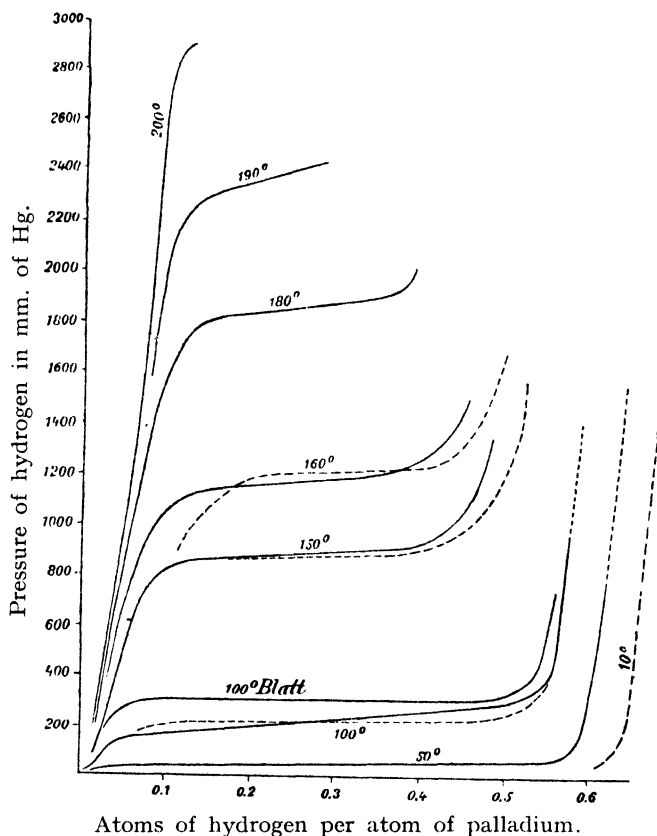


Fig. 95.--Isotherms for Hydrogen and Palladium Sponge, showing changes of Pressure in mm. Hg for different amounts of Hydrogen taken up in Atoms of Hydrogen per Atom of Palladium. The Isotherm marked "Blatt" is for foil at 100°. — Hoitsema; ---- Roozeboom.

"Below 0° C., adsorption only. 0° — 150° C., adsorption followed by absorption. Above 150° C., absorption only."

¹ J. B. Firth, *J. Chem. Soc.*, 1920, **117**, 171.

This is deduced from observations on the time factor of sorption at various temperatures ¹ by Holt, Edgar and Firth.² They agree with Sieverts ³ and others that there are probably two forms of the metal, one amorphous and unstable as in palladium black, the other crystalline, and that the two may co-exist in variable quantities. Diffusion into the crystalline variety becomes noticeably rapid above room temperature, whereas the amorphous form is effectively permeable at all temperatures. Action of hydrogen tends to disrupt palladium with formation of the amorphous variety, rendering it porous. This may be also ascribed to the intense local strains set up by the expansion of the space lattices (see this chapter, page 302). Atomic hydrogen seems to be the effective agent.

The most carefully established isotherms are those of Gillespie and Hall.⁴ They quote the results of Lambert and Gates,⁵ who worked with palladium sponge at 75°, 103° and 120° C., as proving abundantly that true reversible equilibrium, independent of time, cannot be attained by operating isothermally at ordinary temperatures on any preparation of palladium whatsoever. Lambert and Gates' curves show a remarkable hysteresis even although their sponge was constant in properties throughout three years, and the initial adjustments of sorption were always rapid. Withdrawal of hydrogen

¹ W. Ramsay (*Phil. Mag.* (5), 1894, **38**, 206) found that the diffusion of hydrogen through palladium was extremely slow at 237° C.

² A. Holt, E. C. Edgar and J. B. Firth, *Z. physik. Chem.*, 1913, **82**, 513; J. H. Andrew and A. Holt, *Proc. Roy. Soc. (London)*, A, 1913, **89**, 170; A. Holt, *Proc. Roy. Soc. (London)*, A, 1914, **90**, 226; J. H. Andrew, *Trans. Farad. Soc.*, 1919, **14**, 232; J. B. Firth, *J. Chem. Soc.*, 1920, **117**, 171; 1921, **119**, 1120; J. Aharoni and F. Simon (*Z. physik. Chem.*, Abt. B, 1929, **4**, 188) nevertheless, without reference to the existing evidence that diffusion does not occur and that some hydrogen is locked up at room and lower temperatures in compact palladium, conclude that, since the sorption at — 185° is as rapid as at room temperature, the hydrogen is relatively freely mobile through the space lattice of the palladium like gaseous electrons.

³ A. Sieverts, *Z. physik. Chem.*, 1914, **88**, 103.

⁴ L. J. Gillespie and F. P. Hall, *J. Am. Chem. Soc.*, 1926, **48**, 1207.

⁵ R. Lambert and S. F. Gates, *Proc. Roy. Soc. (London)*, A, 1925, **108**, 456.

gave a definite repeatable lower limit for the pressure values, the middle portion of the isotherm being constant within 10 mm.

Gillespie and Hall repeatedly evacuated palladium black at 400° C., cooling and admitting hydrogen, and re-evacuating at 400° C. They approached equilibrium by removing some hydrogen, heating the system a short time at 360° C., and restoring the original temperature. Thereafter the isotherms could be followed reversibly, if between each measurement the palladium was heated to 360° for 2-4 minutes. Two

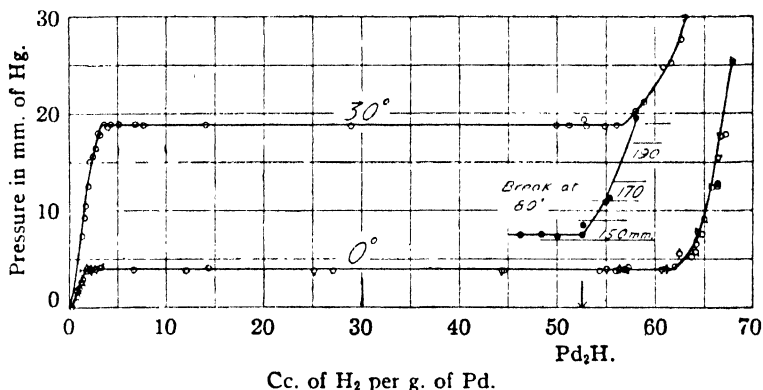


Fig. 96.—Isotherms of Gillespie and Hall for the Sorption of Hydrogen by Palladium. Inset shows break at 80° with separate pressure but same composition scale. Plain circles on 0° Isotherm represent Palladium A; Circles with one mark indicate Palladium B; Circles with two marks indicate the same result with both preparations.

different preparations of palladium black thus gave isotherms at 0°, identical with each other and with the first part of that obtainable without heating. Their isotherms are reproduced in figs. 96¹ and 97.²

The specific heat of sorbed hydrogen or "hydrogenium"

¹ L. J. Gillespie and F. P. Hall, *J. Am. Chem. Soc.*, 1926, **48**, 1212, fig. 2.

² L. J. Gillespie and F. P. Hall, *J. Am. Chem. Soc.*, 1926, **48**, 1213, fig. 3.

was measured calorimetrically by Dewar ¹ by subtracting that of the original palladium. The results depended upon the mode of comparison but lay between 3.3 and 5.9 calories per gram of sorbed hydrogen.

The paramagnetism of palladium was shown by Biggs ² to fall off at 15° C. almost linearly with the addition of hydrogen between 4 volumes and 550 volumes. This was interpreted

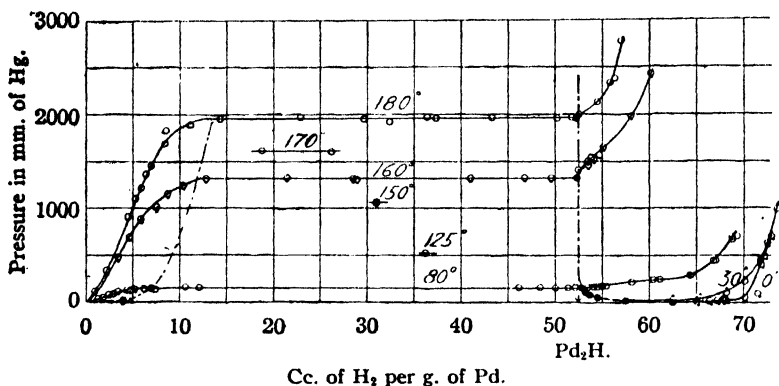


Fig. 97.—Gillespie and Hall's Isotherms for the Sorption of Hydrogen by Palladium at relatively high pressures. The solid circles and the broken lines show the compositions of the coexistent solid phases as functions of the pressure.

as probably due to some interaction of the hydrogen and palladium.

Oxley ³ repeated the comparison of uncharged palladium with that containing hydrogen at atmospheric pressure. Both interpret the loss in magnetic susceptibility as ascribable to loose chemical interaction between hydrogen and palladium because the change is too great to be explained as the additive effect of the diamagnetic hydrogen molecules to the para-

¹ J. Dewar, *Trans. Roy. Soc. Edin.*, 1876, **27**, 170.

² H. F. Biggs, *Phil. Mag.* (6), 1916, **32**, 139. T. Graham (*J. Chem. Soc.*, 1869, **22**, 430) found the opposite effect with crystalline palladium. This possibly may be due to the fact that the specific susceptibility of palladium black is five times greater than that of crystalline palladium.

³ A. E. Oxley, *Proc. Roy. Soc. (London)*, A, 1922, **101**, 264.

magnetic palladium, and the free hydrogen atom of either Bohr or Oxley should have an effect in the opposite direction.

The measurements have been extended by Aharoni and Simon¹ at 0° C. and — 196° C., and they come to the same conclusion. The magnetic susceptibility falls almost linearly over the whole range of sorption somewhat beyond the composition Pd₂H and thereupon is unaffected by further additions of hydrogen. The two possibilities are weakly paramagnetic Pd₂H or diamagnetic PdH. Oxley, like Linde and Borelius,² favours the latter but suggests that the unstable compound is perhaps "even a mere wandering of the hydrogen atom over the 'surfaces' of the palladium atoms, to which the former temporarily attach themselves." Aharoni and Simon adopt the latter view as to the relatively free movement of the hydrogen atoms.³

The most recent well-informed authority on the X-ray study of palladium and hydrogen is Hanawalt.⁴ He finds that

"X-ray absorption pictures of the L_{III} limit of palladium show that the presence of the hydrogen causes a shift of the main edge of 0.87 X.U. toward shorter wave lengths, and the occurrence of a secondary absorption 10 X.U. toward shorter wave lengths. This is taken to mean that the hydrogen is in chemical combination with the palladium. The appearance of the edge may be explained on the hypothesis that it is the superposition of two absorption edges, one due to the molecule PdH and the other due to the atom Pd."

He concludes that the points in the space lattice are occupied alternately by palladium atoms and PdH molecules.⁵ The crystalline phase of palladium forms a face centred cubic

¹ J. Aharoni and F. Simon, *Z. physik. Chem.*, Abt. B, 1929, **4**, 188.

² J. O. Linde and G. Borelius, *Ann. der Physik* (4), 1927, **84**, 747.

³ See also G. Tammann, *Nachr. kgl. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 1918, p. 227.

⁴ J. D. Hanawalt, *Phys. Rev.* (2), 1929, **33**, 444.

⁵ G. Tammann and J. Schneider (*Z. anorg. allgem. Chem.*, 1928, **172**, 54) showed that addition of gold, silver or copper to a palladium cathode reduced to nothing the hydrogen taken up during electrolysis as soon as half of the palladium atoms had been replaced.

lattice¹ with a value for a_0 of 3.885² for pure palladium, increasing linearly with addition of hydrogen to 4.017³ at about the composition Pd_2H ; the latter spacing seems to be of particular significance as it is spontaneously re-established after further saturation, losing hydrogen just to but not beyond this point if charged electrolytically rather than if merely exposed to hydrogen. Cathodic sputtering gave values not exceeding 3.920,⁴ and not shrinking during two years' exposure to air at 20° C. It was shown that the micro crystals were broken up by the sorption of hydrogen. This is completed by the usual supercharging during the electrolytic process. Residual mechanical strain is the probable cause of breakdown below the composition Pd_2H . The compound PdH should be very similar to the atom Ag; addition of the latter to palladium likewise increases the space lattice. If the space lattice of the alloy is less than that of the alloy with about 75 per cent silver, the alloy will take up enough hydrogen to bring it to that value.⁵

That palladium is not the only metal showing this particular

¹A. W. Hull, *Phys. Rev.* (2), 1917, **17**, 571.

²L. W. McKeehan (*Phys. Rev.* (2), 1923, **21**, 334) obtained for pure palladium 3.90 and for palladium saturated with hydrogen from 4.000 to 4.039, 4.036 being suggested as corresponding to Pd_2H .

³J. O. Linde and G. Borelius (*Ann. der Physik* (4), 1927, **84**, 747) obtained 4.034 at 20° C. and 4.032 at 90° C. by electrolysis, supersaturation giving up to 4.094 Å. They could not get larger values than 3.978 by exposure to hydrogen but they used a different and smaller camera for the latter measurements. M. Yamada's lesser limits (*Phil. Mag.* (6), 1923, **45**, 241), although confirmed by his pupil, A. Osawa (*Science Repts. Tôhoku Imp. Univ.* (1), 1925, **14**, 45), are ascribable to impurities giving foreign atoms in portions of the space lattice. Yamada had rejected the hypothesis of any chemical combination because of the gradual change of the position of the X-ray lines, instead of replacement of the fixed set by a second constant set, but L. W. McKeehan demonstrated the latter. F. Krüger and A. Sacklowski (*Ann. der Physik* (4), 1925, **78**, 73) found 4.00 as their largest value. Palladium and silver have a very similar space lattice and those of palladium-silver alloys are intermediate.

⁴A. Bredig and R. Allolio (*Z. physik. Chem.*, 1927, **126**, 41) obtained 3.991.

⁵F. Krüger and A. Sacklowski, *Ann. der Physik* (4), 1925, **78**, 82.

form of isotherm with hydrogen is demonstrated in fig. 98.¹ Sieverts and his collaborators (see this chapter, page 293, footnote 3) found that the metals of the rare earths and of the titanium and vanadium groups are of the same type as palladium. The initial portion of the 800° isotherms for cerium and for an alloy with lanthanum are given in fig. 98¹ and the remaining parts of the isotherms for cerium in fig. 99.² The 600° isotherm for titanium is similar, whereas those at higher temperatures have the more usual form.

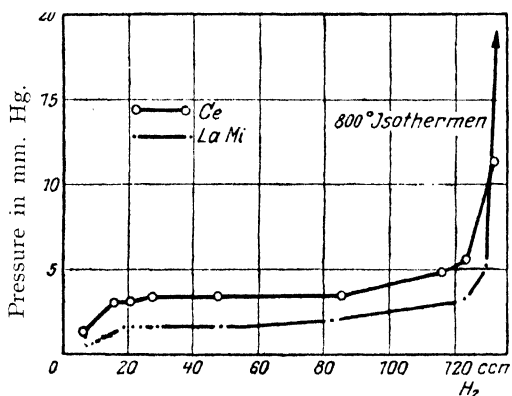


Fig. 98.—Initial Portion of the Isotherms for Hydrogen with Cerium and with an Alloy of Lanthanum at 800° C., showing the Resemblance to the behaviour of Palladium with Hydrogen. The sorption is expressed in cubic centimetres of hydrogen (at N.T.P.) per gram of metal.

Sorption of sulphuretted hydrogen by palladium black was found by Maxted³ to interfere with the sorption of hydrogen. His palladium black was freed from oxygen with hydrogen and evacuated at 100° C. It was capable of sorbing 68.5 c.c. (at N.T.P.) of hydrogen per gram of palladium. When sulphuretted hydrogen was used instead, the amount sorbed increased from 11.5 c.c. (at N.T.P.) after one minute to 22.6

¹ A. Sieverts, *Z. Metallkunde*, 1929, **21**, 41, fig. 9.

² A. Sieverts, *Z. Metallkunde*, 1929, **21**, 41, fig. 10.

³ E. B. Maxted, *J. Chem. Soc.*, 1919, **115**, 1050; 1920, **117**, 1280.

c.c. after 18 hours and 42.6 c.c. after three weeks. Thereafter the hydrogen sulphide could not be removed by evacuation at room temperature, but at 100° the gas extracted consisted almost entirely of hydrogen, the sulphur being left in the palladium. Such sulphur does not interfere with the sorption of hydrogen. On the other hand, only 8 c.c. of hydrogen sulphide per gram of palladium is sufficient to prevent the sorption of hydrogen. Smaller amounts of hydrogen sulphide diminish the sorption of hydrogen in linear proportion. Sorption of hydrogen was similarly diminished in linear pro-

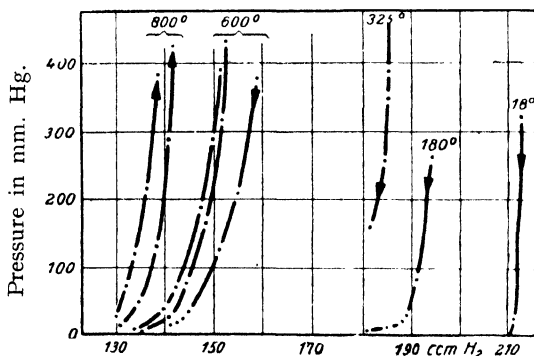


Fig. 99.—Continuation of the Isotherms of Cerium and Hydrogen at higher Pressures and various Temperatures.

portion to the lead ¹ content of palladium that had been exposed to dilute solutions of lead acetate, and the rate of sorption of hydrogen changed from being nearly instantaneous to being extremely slow. The catalytic activity of the palladium as measured by the rate of hydrogenation of oleic acid was likewise reduced almost linearly up to a point at which the greater part of the activity was suppressed, but it required less than one-eighth as much lead to diminish the catalytic activity by one-half as it took to reduce the sorptive power to one-half, showing that sorption, unlike catalysis, was not confined to the surface. This interpretation is borne out by the fact that

¹ E. B. Maxted, *J. Chem. Soc.*, 1921, **119**, 1280.

the catalytic activity varies with the fineness of division of the catalyst, whereas the effect on sorption does not vary.

SORPTION OF WATER AND OTHER VAPOURS ON SMOOTH METALLIC SURFACES

The method developed by McHaffie and Lenher¹ for estimating the sorption of vapours by observing deviations from the perfect gas law when a vapour was cooled in a bulb made of the material to be studied through the range of temperatures in the neighbourhood of the saturation pressure of the liquid has been applied also to surfaces of platinum, amalgamated platinum and amalgamated silver.²

A surface of platinum polished with rouge indicated thick films up to 39 molecules or 113 Å. deep of water, and the sorption is therefore much less than on glass. However, these films began to appear rather abruptly at a high relative humidity. The heats of formation of these films are similar to the heats of condensation to liquid water in bulk. The adsorption potential diminished linearly with the thickness of the film. Benzene films were indicated up to 159 molecules or 930 Å. deep. Such polished surfaces of platinum have been shown by X-ray studies to be amorphous³ and

¹ See Chapter VII, page 224. R. Strömberg (*Kgl. Svenska Vetenskapssakad. Handl.* (3), 1928, **6**, No. 2, 116, 117) ascribes to their work great experimental inaccuracy.

² I. R. McHaffie and S. Lenher, *J. Chem. Soc.*, 1925, **127**, 1568; S. Lenher, *J. Chem. Soc.*, **1926**, 1790; **1927**, 276; S. Lenher and I. R. McHaffie, *J. Phys. Chem.*, 1927, **31**, 719; J. C. W. Frazer, W. A. Patrick and H. E. Smith, *J. Phys. Chem.*, 1927, **31**, 899; J. W. Smith, *J. Chem. Soc.*, **1928**, 2045; G. H. Latham, *J. Am. Chem. Soc.*, 1928, **50**, 2994.

³ J. C. W. Frazer, W. A. Patrick and H. E. Smith, *J. Phys. Chem.*, 1927, **31**, 898. They state "platinum is known to be activated by heating in air; this we believe is due to the formation of finely divided platinum on its surface". C. G. Fink (*Dissert.*, Leipzig, 1907, p. 52) estimated that the film of sulphur trioxide sorbed simultaneously with some oxygen and sulphur dioxide was 12 Å thick, not allowing, however, for the roughening of the platinum gauze through its repeated use as a catalyst.

it may be added that they are very likely to be contaminated with impacted polishing material.

To obviate criticism based upon the uncertainties as to the state and nature of polished platinum surfaces, Smith¹ employed a bulb of platinum which had been amalgamated with sodium amalgam. The surface was reproducible and permanent in the presence of water and benzene but not when exposed to the air. The saturated vapour pressure indicated for water was 1.3 mm. low and for benzene 1.6 mm. low for unknown reasons. The films indicated were up to 42 molecules deep for water and up to 312 for benzene.

Latham² used platinum amalgamated by electrolysis and obtained, like Smith, indicated films up to 28 or 33 molecules deep for water. Finally, Latham employed a similarly amalgamated bulb of silver and here found that the sorption of water vapour could not exceed one molecule deep. He concludes that the amalgamated platinum surfaces were not smooth.

Chapman³ made an incidental observation that at 120°C. and at high relative pressure the sorption of toluene upon gold foil appeared to be equivalent to a liquid layer 500 Å. deep.

SORPTION OF GASES BY AMORPHOUS IRON, NICKEL, COPPER AND OTHER CATALYSTS

Although, as has been seen, the amounts of gases dissolved in various metals are by no means inconsiderable, processes of diffusion are often stilled at room temperature, and the large sorption observed is frequently due to the extensive surfaces rendered accessible in the so-called amorphous as distinguished from the massive crystalline condition.⁴ Another

¹ J. W. Smith, *J. Chem. Soc.*, **1928**, 2045.

² G. H. Latham, *J. Am. Chem. Soc.*, **1928**, **50**, 2994.

³ J. W. McBain, H. P. Lucas and P. F. Chapman, *J. Am. Chem. Soc.*, **1930**, **52**, 2669.

⁴ For example, A. Stock, F. Gomolka and H. Heynemann (*Ber.*, **1907**, **40**, 532) demonstrated such an effect in the sorption of stibine by antimony. A. W. Gauger (*J. Am. Chem. Soc.*, **1925**, **47**, 2280) believes that the importance of mere extent of surface has been much

influence which may enter in here is that demonstrated by Reboul¹ who showed that the chemical reactivity of metallic surfaces, such as those of a wire, increases rapidly with increase of curvature, being most pronounced at points and edges even in large pieces of metal.

The most important single fact about sorption by finely divided metals is that it is highly specific. Thus hydrogen, in spite of its very low boiling point, is far more sorbed by nickel at slightly elevated temperatures than is carbon dioxide, although this disparity is of a lower order of magnitude than that observed with palladium or even with platinum. On the other hand, the sorption of these two gases is roughly equal in the case of copper, while cobalt and iron sorb carbon dioxide much more than hydrogen.

The isobars for hydrogen at one atmosphere with nickel, copper and iron are reproduced in fig. 100.²

The most extensively studied system, on account of its use in hydrogenation, is hydrogen and nickel. Much more hydro-

over-estimated. Thin films of platinum or nickel deposited from the metallic vapour upon Pyrex glass wool were found inactive when tested for catalytic hydrogenation of ethylene. W. Heald (*Physik. Z.*, 1907, **8**, 659), when noting the amounts of gas evolved by metallic cathodes vaporizing in an atmosphere of hydrogen, found that the sorption of hydrogen by the film so formed was instantaneous in the case of aluminium and platinum, iron came next, then cadmium and silver, but zinc sorbed none. S. Valentiner and R. Schmidt (*Ann. der Physik* (4), 1905, **18**, 187) found that such films of aluminium sorb all the noble gases, especially xenon, although the latter may be partially desorbed on heating. K. Czukor (*Chem. Rundschau Mitteleuropa Balkan*, 1927, **4**, 153; through *Chemical Abstracts*, 1929, **23**, 4120) used a magnesium mirror to sorb the gases evolved by electrodes and proposes a formula to show if the vacuum tube is free from gas.

¹ G. Reboul, *Compt. rend.*, 1912, **155**, 1227; 1913, **156**, 1376 (sulphurous gases from rubber upon copper, and chlorine, bromine, iodine, hydrogen sulphide and nitric acid on silver, copper and mercury; he regarded amount of sorption as increasing with degree of curvature). For other references, see J. Wulff, *Nature*, 1929, **123**, 682; L. R. Luce, *Ann. physique* (10), 1929, **11**, 167; see also Chapter VII, page 237, and Chapter XVIII, page 485.

² A. Sieverts, *Z. Metallkunde*, 1929, **21**, 40, fig. 4.

gen is sorbed by nickel ¹ and somewhat more by cobalt ² than by iron, copper and silver, and this is also the order of their catalytic activity in hydrogenation, although iron heads this

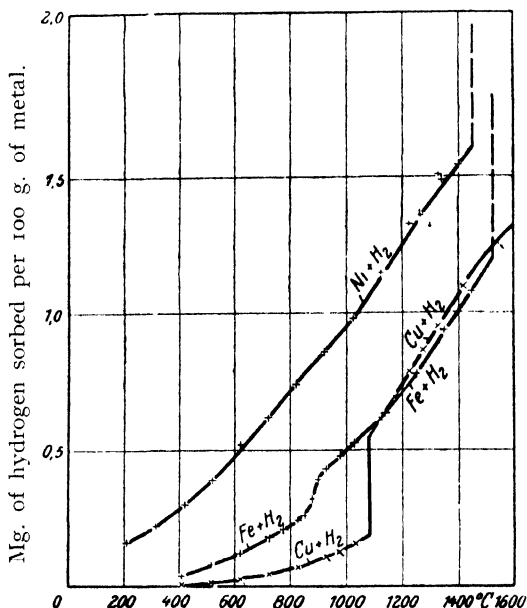


Fig. 100.—Isobars for One Atmosphere of Hydrogen, showing the Number of Milligrams of Hydrogen sorbed by 100 g. of Nickel, Iron and Copper at various Temperatures.

series for ethylene.³ However, such a series possesses but little significance on account of the extremely different sorptive

¹ L. Troost and P. Hautefeuille (*Compt. rend.*, 1875, **80**, 788) found 0.2 volumes by one volume of nickel; G. Neumann and F. Streintz (*Monatsh.*, 1891, **12**, 657), about 17; G. P. Baxter (*Am. Chem. J.*, 1899, **22**, 360), 2–10; M. Mayer and V. Altmayer (*Ber.*, 1908, **41**, 3062), up to 50 volumes at 360°C.; A. Sieverts (*Z. physik. Chem.*, 1911, **77**, 591), 0.18 at 200°C. and 1 at 1,000°C.

² W. Hempel and H. Thiele (*Z. anorg. Chem.*, 1896, **11**, 93) found none in their preparation of cobalt.

³ R. N. Pease and L. Stewart, *J. Am. Chem. Soc.*, 1927, **49**, 2783; H. S. Taylor and R. M. Burns, *J. Am. Chem. Soc.*, 1921, **43**, 1273.

powers of the specimens of any one metal as prepared by different investigators. Baxter¹ showed that the sorptive capacity of nickel and cobalt for hydrogen depended upon

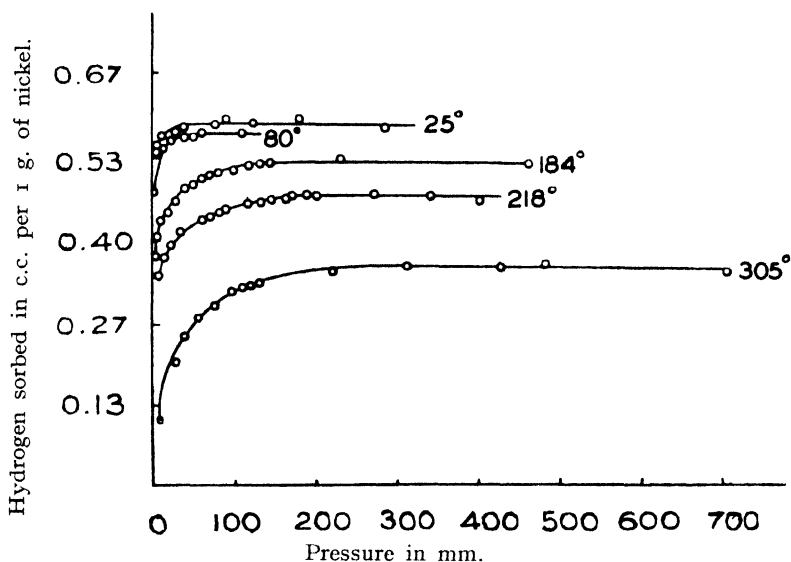


Fig. 101.—Gauger and Taylor's Isotherms for the Sorption of Hydrogen in c.c. (at N.T.P.) per Gram of Nickel.

the temperature of preparation and that to which they were subsequently heated.

Fig. 101² shows the isotherms obtained by Gauger and Taylor with a nickel oxide incompletely reduced by hydrogen

¹ G. P. Baxter, *Am. Chem. J.*, 1899, **22**, 351. Copper and silver contained but little hydrogen. Cobalt, reduced at 400°–500° C., contained about 20 volumes of hydrogen. If prepared in the presence of much sodium chloride, it contained 48 volumes and spontaneously oxidized in the air. Finely divided cobalt slowly sorbed hydrogen at room temperature.

² A. W. Gauger and H. S. Taylor, *J. Am. Chem. Soc.*, 1923, **45**, 924, fig. 1. Their calculated heat of sorption is not referred to in Chapter XIV because it is not supported by later work.

and evacuated at 300° C. ¹; this sorption could be increased tenfold and rendered nearly independent of temperature by supporting or spreading out the nickel on diatomaceous earth or diatomite brick unless heated at too high a temperature. Unsupported nickel was least stable in accordance with the conceptions suggested by Baxter,² and the sorptive properties of all these catalysts depend upon their previous history.³

It will be seen from fig. 101 that the amount of sorption at 305° C. was only about half that at 25° C. From this Terwen ⁴ concluded that the sorbed hydrogen occurred as atoms at the higher and as molecules at the lower temperature. However, the experimental results of Gauger and Taylor may be compared with those of Nikitin in fig. 102 ⁵ in which there is no

¹ O. Schmidt (*Z. physik. Chem.*, 1925, **118**, 226) showed that evacuation removes only between 33 and 73 per cent of the hydrogen from nickel at 200° C., 65 to 88 per cent at 300° C., and still only 91 to 96 per cent at 400° C.; however, all the hydrogen can be removed from nickel by oxidation.

² G. P. Baxter, *Am. Chem. J.*, 1899, **22**, 351.

³ C. F. Fryling (*J. Phys. Chem.*, 1926, **30**, 820) prepared ten different nickel catalysts and noted that their sorptive power for hydrogen at 0° C. was not an exact criterion of catalytic activity. O. Schmidt (*Z. physik. Chem.*, 1925, **118**, 235) found approximate proportionality between sorption of hydrogen at 20°, catalytic activity and superficial area of a number of nickel catalysts. He also (page 216) adduces photomicrographs showing the progressive sintering and coarsening of nickel prepared at successively higher temperatures.

⁴ J. W. Terwen, *Chem. Weekblad*, 1924, **21**, 386.

⁵ N. Nikitin, *Z. anorg. allgem. Chem.*, 1926, **154**, 137, fig. 4; *J. Russ. Phys.-Chem. Soc.*, 1926, **58**, 1081. The isotherm at 110° was intermediate between those for 19° and 336°. Carbon dioxide was sorbed at 14° to about the same extent as hydrogen but this fell to about one-sixth at 335° C. A fraction of the sorption at 14° was irreversible. N. I. Nikitin and V. I. Sharkov (*J. Russ. Phys.-Chem. Soc.*, 1926, **58**, 1095) found that nickel powder did not sorb any gases except when mixed with alumina; the latter alone sorbed carbon dioxide but not hydrogen. Cobalt was variable but could be made as active as nickel, and even more so for carbon dioxide. Other powders studied with hydrogen, carbon dioxide and ammonia were nickel, cobalt, iron, silver, copper and lead. The latter two sorbed practically nothing. Silver sorbed some hydrogen but much more carbon dioxide (2.6 c.c. at N.T.P. by one gram of silver at - 81° C.).

such difference between the results for room temperature and 336° C. Russell and Taylor¹ themselves did not confirm the position of these curves but found a maximum sorption at

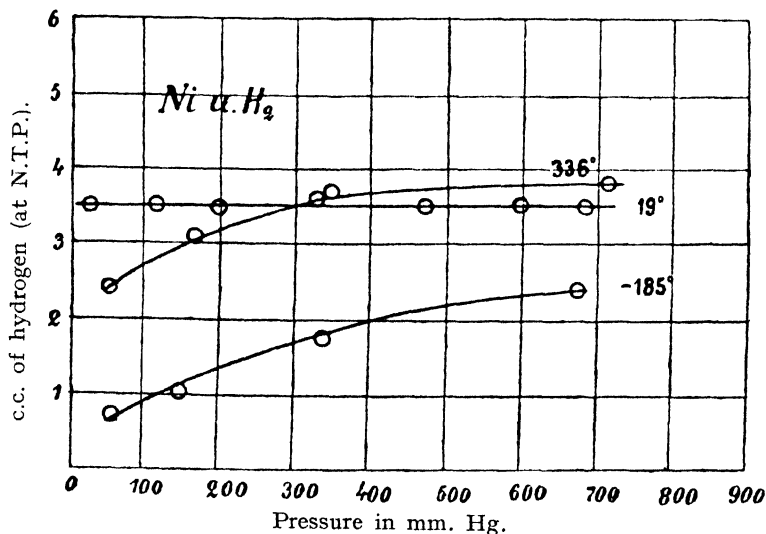


Fig. 102.—Nikitin's Isotherms for Nickel and Hydrogen; c.c. (at N.T.P.) per 5 g. of Nickel.

110° with the value at 218° C. exceeding that at 0° C. Taylor and Burns² likewise did not confirm Gauger's results, but

¹ W. W. Russell and H. S. Taylor, *J. Phys. Chem.*, 1925, **29**, 1333. Also measurements of carbon dioxide which was less sorbed than hydrogen except after addition of thoria. Nitrogen was not measurably sorbed by nickel. The experiments were extended to nickel with thoria, with and without the support of pumice.

² H. S. Taylor and R. M. Burns, *J. Am. Chem. Soc.*, 1921, **43**, 1277. The sorption of carbon monoxide and of ethylene by nickel is fully comparable with that of hydrogen, carbon dioxide being much less. Other measurements were made with copper, cobalt, iron, palladium and platinum and the same gases. The relative sorption of these gases varies specifically from case to case; see also H. S. Taylor, *Colloid Symposium Monograph* (Wisconsin, 1923), 1923, **1**, 97. Mixtures of hydrogen and nitrogen were studied with nickel. Cobalt at 25° sorbed 0 to 1.7 volumes of hydrogen, 0.35 of ethylene, 1.6 to 7.4 of carbon monoxide, and 0.5 to 2 of carbon dioxide.

obtained results with three specimens, differing amongst themselves, one showing a tendency to increase by 40 per cent at 218°C. as compared with 25°C. Nikitin¹ obtained a similar diagram, with even greater diminution between 14°C. and 335°C. with carbon dioxide which, of course, cannot be explained as due to atoms and molecules.

The effect of temperature upon the isotherms for hydrogen

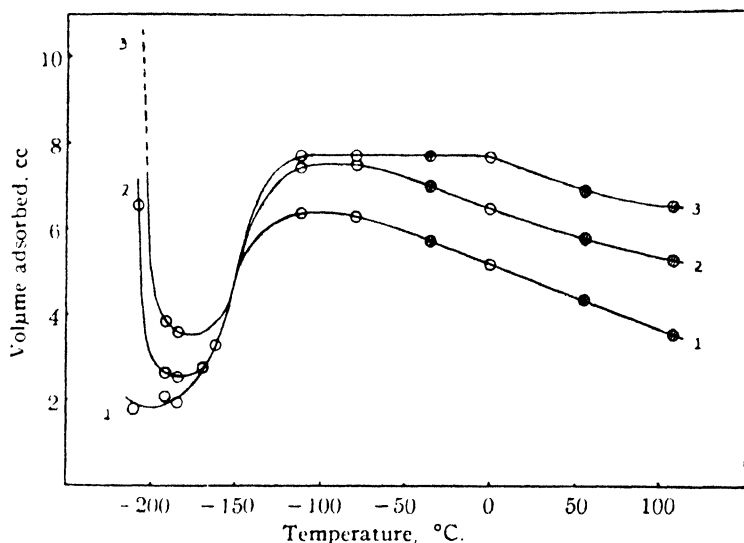


Fig. 103.—Benton and White's Isobars for Hydrogen on Nickel; c.c. (at N.T.P.) per 23.68 g. of Nickel. Curve 1, at 2.5 cm.; Curve 2, at 20 cm.; Curve 3, at 60 cm. Pressure.

and nickel was investigated more fully by Benton and White² whose isotherms are not nearly as flat as those of Gauger and Taylor. They confirmed the difference found by Nikitin between results at liquid air and room temperatures. How-

¹ N. Nikitin, *Z. anorg. allgem. Chem.*, 1926, **154**, 140; *J. Russ. Phys.-Chem. Soc.*, 1926, **58**, 1081.

² A. F. Benton and T. A. White, *J. Am. Chem. Soc.*, 1930, **52**, 2325. Results with copper resemble those with nickel in spite of much smaller sorption. However, sorption of carbon monoxide by copper increases regularly with lowering of temperature.

ever, the effect of temperature is rather complicated as is illustrated by their isobars in fig. 103.¹

Fig. 104² is chosen for comparison with that of Nikitin (fig. 102) and also to illustrate the peculiar progression of the low temperature isotherms of Benton and White. The experiments are rather slowly reversible at 0° C., being accompanied by some slow sinking of hydrogen into the nickel. When

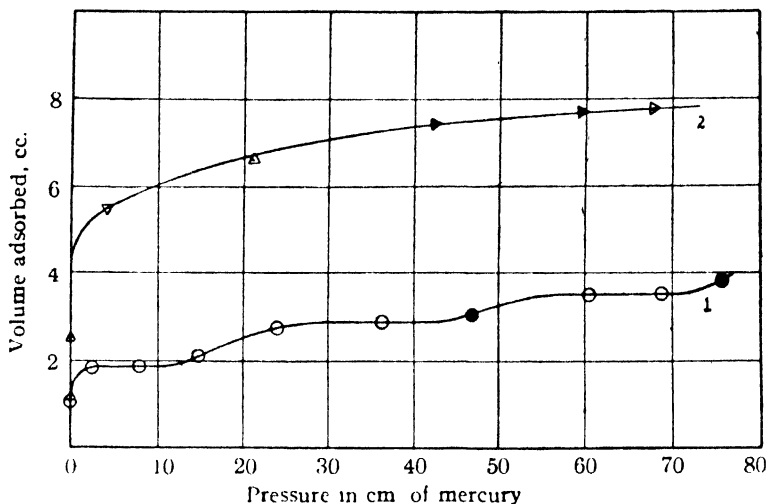


Fig. 104.—Benton and White's Sorption Isotherms for Hydrogen and Nickel; c.c. (at N.T.P.) per 23.1 g. of Nickel. Curve 1, at -183° C.; Curve 2, at 0° C.

¹ A. F. Benton and T. A. White, *J. Am. Chem. Soc.*, 1930, **52**, 2332, fig. 5. See also A. de Hemptinne (*Z. physik. Chem.*, 1898, **27**, 429; *Bull. sci. acad. roy. Belg.* (3), 1898, **36**, 155) who brought hydrogen, or carbon monoxide, into equilibrium with platinum black at -78° C. and then allowed the system to warm gradually to 15° C. The gas sorbed at -78° C. was at first gradually evolved on warming, up to a temperature of about -40° C., after which the sorption rapidly increased to a greater value than at -78° C. Similar behaviour was observed with carbon monoxide and palladium; here carbon monoxide diminished the sorption of hydrogen.

² A. F. Benton and T. A. White, *J. Am. Chem. Soc.*, 1930, **52**, 2331, fig. 4.

nickel which has sorbed its quota at 0°C . is cooled to -186°C ., in spite of the results in figs. 102 and 104, almost as much more hydrogen is sorbed as if the nickel were initially free from hydrogen.

Benton and White adapt Terwen's explanation to this lower temperature range. Sorption at -183°C . is almost instan-

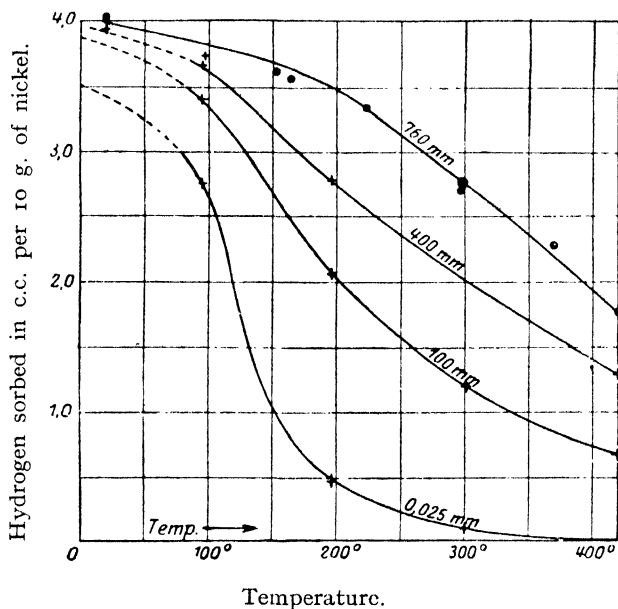


Fig. 105.—Schmidt's Isobars for Hydrogen and Nickel. ⊕, ●, + = before, after and during Isothermal Measurement, respectively.

taneous and then remains constant for at least 70 hours, and is completely and quickly reversible in its response to pressure changes. This is the purely physical type of sorption of hydrogen molecules and is confined to temperatures below -110°C . They venture the suggestion that the surface at temperatures between -110°C . and 0°C . is entirely covered with a single layer of activated hydrogen, probably atomic,

held by chemical forces.¹ Such chemisorption is less pronounced at still lower temperatures but has not entirely disappeared even at -200°C . Their discussion makes no reference to the work of Schmidt,² whose isobars are given in

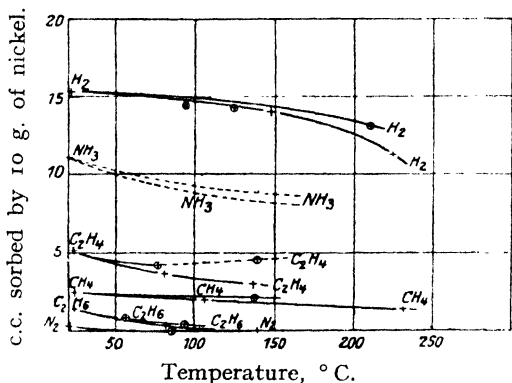


Fig. 106.—Schmidt's Isobars at 760 mm. for various Gases and Nickel.

¹ A. W. Gauger (*J. Am. Chem. Soc.*, 1924, **46**, 674) considered that a study of critical potentials of hydrogen in presence of nickel favoured this view. J. H. Wolfenden (*Proc. Roy. Soc. (London)*, A, 1926, **110**, 464) severely criticized the experiments of Gauger, but concluded from a modified procedure with nickel and with nickel and copper catalysts that atomic hydrogen was present upon the surface in each case. W. Schlenk and T. Weichselfelder (*Ber.*, 1923, **56B**, 2230) showed that nickel in colloidal suspension in anhydrous ether could sorb 3,400 volumes of hydrogen. This corresponds to four atoms of hydrogen to one of nickel or the formula, NiH_4 , and the product surpasses in hydrogenating power all other nickel catalysts. On drying in hydrogen, the solid has the composition NiH_2 . The authors conclude that the catalytic activity of nickel is due to the formation of hydride. B. Kubota and K. Yoshikawa (*Sci. Papers Inst. Phys. Chem. Research (Japan)* 1925, **3**, 33 and 223; *Japan. J. Chem.*, 1925, **2**, 45) investigated the effects of thiophene, ethyl sulphide and hydrogen sulphide upon catalytic nickel and copper and concluded that if, for example, sorption of hydrogen sulphide occurred only by combination with surface atoms, most of the nickel atoms were upon the surface.

² O. Schmidt, *Z. physik. Chem.*, 1925, **118**, 211; 1928, **133**, 295.

fig. 105¹ and show some agreement with those of Gauger and Taylor rather than with Nikitin. It therefore remains an open question as to why the sorption should so fall off above room temperature (perhaps due to sintering), whilst being at each temperature so little affected by pressure change. Probably, however, the isotherms of Gauger and Taylor were too constant in this respect. Schmidt² found that at higher temperatures above a certain pressure the sorption increased in proportion to the square root of the pressure.

An idea of the relative sorption of various gases by nickel may be obtained from fig. 106.³ Its sorption of water vapour is practically negligible.⁴

Copper catalysts have been studied by several authors in addition to those to whom incidental reference has already been made. Dew and Taylor obtained the following results for the volume in cubic centimetres at N.T.P. sorbed by one gram of metal presumably at one atmosphere pressure, nitrogen not being sorbed at all.⁵

¹ O. Schmidt, *Z. physik. Chem.*, 1925, **118**, 211, fig. 4. Schmidt ascribes the decrease in his isobars at higher temperatures as due to sintering, and points out that the large increases with temperature found by A. Sieverts were due to his having used nickel which had already been sintered (A. Sieverts, *Z. physik. Chem.*, 1907, **60**, 129; 1911, **77**, 591; A. Sieverts and J. Hagenacker, *Ber.*, 1909, **42**, 338).

² O. Schmidt, *Z. physik. Chem.*, 1925, **118**, 195; compare B. Foresti (*Gazz. chim. ital.*, 1929, **59**, 243) who adduces isotherms for hydrogen, ethylene and ethane at 20°C. and shows that far more sorption is observed, especially with hydrogen, if the preliminary evacuation is carried out at 250°C. rather than at 21°C. He argues that some of the adsorption is molecular although that of hydrogen on the most active centres is atomic.

³ O. Schmidt, *Z. physik. Chem.*, 1928, **133**, 295, fig. 3. He also gives isobars for other nickel preparations including some containing such admixtures as iron, aluminium, barium, vanadium, and also graphs similar to those referred to in Chapter III, page 56, and Chapter IV, page 119.

⁴ M. Guichard, *Bull. soc. chim.* (4), 1922, **31**, 650.

⁵ W. A. Dew and H. S. Taylor, *J. Phys. Chem.*, 1927, **31**, 281. One gram of sodium sorbed 0.16 c.c. of ammonia. One gram of a "50-50 mixture" of iron and molybdenum sorbed 2.30 c.c. of ammonia at 25°C., 0.0032 c.c. of hydrogen at 25°C., but 0.0 c.c. at 100°C.

TABLE 41

Sorption of Ammonia and Hydrogen by Amorphous Metals

		0°	110°	218°	305°	444·6°
Copper	¹ H ₂	0·155	0·134	0·093	—	—
	NH ₃	0·458	0·187	0·112	—	—
Nickel	NH ₃	0·875	0·0457	0·100	0·065	—
Iron	H ₂	0·0074	0·0028	0·0195	0·0116	—
	NH ₃	0·175	0·0669	0·036	0·0084	—

Their isotherms for ammonia on copper, nickel, iron and iron-molybdenum continue to rise rapidly with increasing pressure.

Isotherms for five gases with copper are given by Pease ² and reproduced in fig. 107.³ The best formulation is a slight modification of that of Langmuir. The order of sorption varies with the temperature. Very small amounts of mercury decrease the sorptive power of the copper for all of the gases, but by very unequal amounts. Heating diminished them differently. X-ray analysis showed that the active copper catalyst had the same arrangement and spacing of atoms as ordinary massive copper, although its apparent density was 2·5 per cent less than that of massive copper.

The sorption of hydrogen, carbon monoxide and ethylene on a copper catalyst has been studied by Griffin ⁴ who also obtained the unexpected result that the sorption of hydrogen and of ethylene at low pressures is increased by the presence of carbon monoxide on the catalyst. Further, this effect is

¹ Melsens (quoted by Dumas, *Ann. chim. phys.* (3), 1843, **8**, 205) found 19·8 volumes of hydrogen sorbed by one volume of copper, whereas W. Hampe (quoted by H. Fresenius, *Z. anal. Chem.*, 1874, **13**, 362) and H. S. Taylor and R. M. Burns (*J. Am. Chem. Soc.*, 1921, **43**, 1280) found none.

² R. N. Pease, *J. Am. Chem. Soc.*, 1923, **45**, 1196, 2296; R. N. Pease and L. Stewart, *J. Am. Chem. Soc.*, 1925, **47**, 1235.

³ R. N. Pease, *J. Am. Chem. Soc.*, 1923, **45**, 2297, fig. 1. A. Sieverts and W. Krumbhaar (*Ber.*, 1910, **43**, 893) found that no carbon monoxide was sorbed by copper, whereas H. S. Taylor and R. M. Burns (*J. Am. Chem. Soc.*, 1921, **43**, 1280) found that 0·6 volumes were sorbed by one volume of copper. They likewise found that copper took up 0·65 volumes of ethylene.

⁴ C. W. Griffin, *J. Am. Chem. Soc.*, 1927, **49**, 2137.

reversed at high pressures. The hydrogen and ethylene in the enhanced sorption due to carbon monoxide are not in activated form.

The sorption of hydrogen, carbon monoxide and their

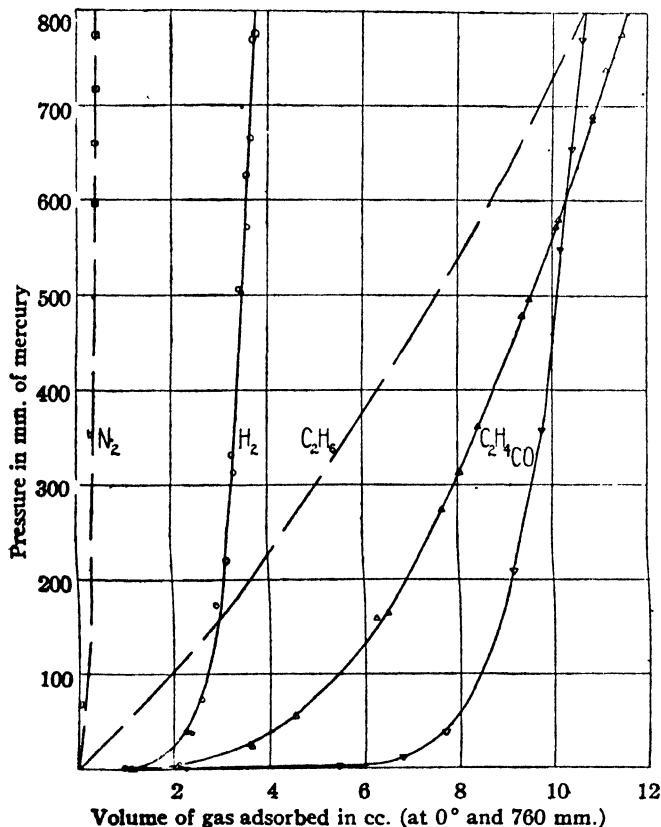


Fig. 107.—Pease's Isotherms for Sorption by a Copper Catalyst at 0° C. ; c.c. (at N.T.P.) Sorbed by 117 g. of Copper.

mixtures by copper and by copper containing 0.2 per cent palladium has been studied by Hurst and Rideal.¹ The addition

¹ W. W. Hurst and E. K. Rideal, *J. Chem. Soc.*, 1924, **125**, 669.
F. J. Wilkins and E. K. Rideal (*Proc. Roy. Soc. (London)*, A, 1930,

of palladium to the copper increases the sorption of the carbon monoxide and decreases that of the hydrogen. The observed sorption of the mixed gases is far less than that expected from their sorption separately. A saturation value is obtained with hydrogen at 0° C. above 150 mm. pressure, although the volume of carbon monoxide sorbed at 1 atmosphere is from 8 to 13 times greater.

Iron, finely divided or pyrophoric, has been studied chiefly on account of its importance in the synthesis of ammonia. That prepared from colloidal ferric hydroxide was found by Finzel¹ to be worthless as a catalyst. According to him, sorption of carbon dioxide is not a completely trustworthy criterion for pyrophoric activity, as it is primarily due to residual oxide, although the latter helps to stabilize the particles of iron. His best specimen of pyrophoric iron sorbed 0.55 c.c. of carbon dioxide and 0.95 c.c. of ammonia per gram of iron at 30°. However, Nikitin's² pyrophoric iron sorbed as much as 4 c.c. of carbon dioxide at 18° C. and double this amount at -80° C., the value of the exponent $1/n$ in the classical sorption isotherm at 18° C. being 0.207. Values at 510° C. were again greater than those at 18°, probably on account of solution in the iron. The value for ammonia was 2.3 c.c. at 97° C. and 159 mm., and 10.7 c.c. at -18.2° C. and 556 mm. pressure.³

Nikitin's iron afforded interesting and significant results with hydrogen at various temperatures. There was practically no sorption at 16° C. and at -80° C. and yet it was great at either the temperature of liquid air or at high temperatures, the amounts rising rapidly between 380 and 510° C. These data are shown in fig. 108.⁴

128, 394) and F. J. Wilkins (*Proc. Roy. Soc. (London)*, A, 1930, **128**, 407) have studied the more complicated processes in the sorption of oxygen by copper and the oxidation of the copper.

¹ T. G. Finzel, *J. Am. Chem. Soc.*, 1930, **52**, 150.

² N. Nikitin, *Z. anorg. allgem. Chem.*, 1926, **154**, 130; *J. Russ. Phys.-Chem. Soc.*, 1926, **58**, 1081.

³ N. I. Nikitin and V. I. Sharkov, *J. Russ. Phys.-Chem. Soc.*, 1926, **58**, 1095.

⁴ N. Nikitin, *Z. anorg. allgem. Chem.*, 1926, **154**, 134, fig. 2.

The sorption at -185°C. was of the physical type of adsorption, equilibrium being rapidly attained and the hydrogen being readily removed by subsequent evacuation at room temperature. On the other hand, sorption at high temperatures was of the type of absorption, the hydrogen not

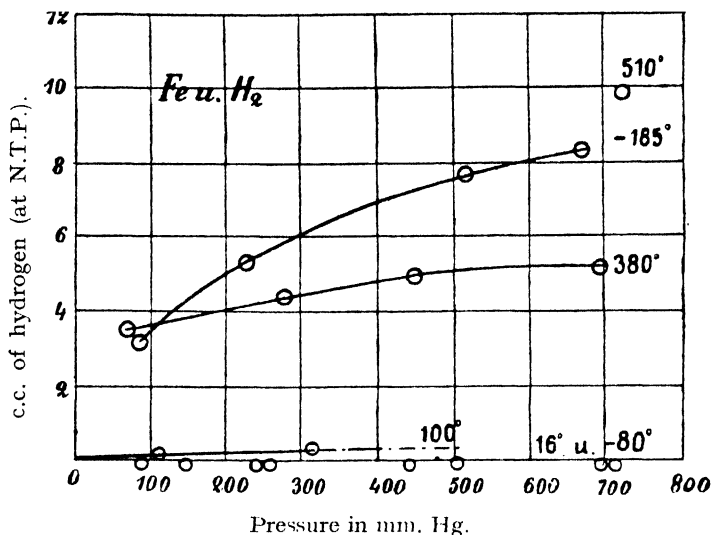


Fig. 108.—Nikitin's Isotherms for Cubic Centimetres of Hydrogen (at N.T.P.) Sorbed by 5 g. of Pyrophoric Iron, showing no Sorption at Room Temperature and Large Sorption well above and below.

being removable by evacuation at room temperature but only beginning to diffuse out above 330°C.

Older workers obtained far smaller values. Thus Taylor and Burns¹ found that one volume of iron sorbed 0.05 volumes² of hydrogen at 25°C. , 0.25 of carbon dioxide, 0.7 of carbon monoxide, and 0.3 of ethylene.

¹ H. S. Taylor and R. M. Burns, *J. Am. Chem. Soc.*, 1921, **43**, 1280.

² A. Sieverts, *Z. physik. Chem.*, 1911, **77**, 591; B. Neumann (*Stahl und Eisen*, 1914, **34**, 252) who found 0.04 volumes of hydrogen at 400°C.

SORPTION BY ALKALI AND ALKALINE EARTH METALS

Aluminium foil, previously evacuated at 300° C., was found by Kälberer and Mark ¹ to sorb carbon dioxide at 0° C. and low pressures according to Henry's law; thereupon after re-evacuation at 300° C., the sorption at 0° C. was much greater and much of it occurred at infinitesimal pressures. This is closely reminiscent of the effect of freeing the surface of charcoal from impurities (see Chapter IV, page 129). The portion sorbed at extremely low pressure at 0°, 45° and 65° C. was insufficient to cover more than 0.3 to 0.4 per cent of the surface.

Finely divided aluminium, obtained by reduction with hydrogen at 300° C. and thoroughly evacuated, was found by Schmidt ² to sorb moderately large amounts of ammonia (1.5 c.c. per gram at 20° C., falling to 0.3 c.c. at 200° C.) and proportionally smaller amounts of carbon dioxide, ethylene, ethane and nitrous oxide over the same temperature range. Methane, hydrogen, nitrogen and argon were much less sorbed at room temperature but the amounts did not diminish as fast on heating.

Sodium commences to sorb or react with hydrogen above 100° C., although the reaction is incomplete, the product having the melting point of sodium.³

REFLECTION OF ELECTRONS FROM METALLIC SURFACES ⁴

What X-ray examination has done and promises to do for the elucidation of the internal structure of crystals, liquids, colloids, liquid crystals and glasses, the reflection of electrons may do for the first few layers of atoms and molecules upon

¹ W. Kälberer and H. Mark, *Z. physik. Chem.*, A, 1928, **139**, 159.

² O. Schmidt, *Z. physik. Chem.*, 1928, **133**, 297.

³ B. Kamienski, *Bull. intern. acad. Polonaise*, **1926A**, 109; through *Chemical Abstracts*, 1927, **21**, 1735.

⁴ For a résumé of the literature on the refraction of electronic radiation, but omitting most of the references to the work of Davisson and Germer on sorption, see E. Rupp, *Ergebnisse der exakten Naturwissenschaften*, 1930, **9**, 79; also in P. Debye, *Elektroneninterferenzen*, Leipzig 1930, S. Hirzel.

their surfaces. Thus Davisson and Germer¹ point out that the intensity of a beam of electron radiation may be reduced 30 or 40 per cent on passing normally through a single layer of atoms; and, as grazing incidence is approached, scattering by the first layer of atoms becomes almost complete. Even hydrogen atoms exhibit a marked effect, in contrast to their negligible influence in X-ray diagrams. It becomes evident that sorption has to be taken carefully into account in all investigations of reflection from surfaces not merely of electronic radiation but also in the reflection of larger particles such as atoms and molecules. The possibilities of the new method have been recognized by many investigators, but the field is still practically untouched.

Davisson and Germer² themselves noted the effect of a gas upon the reflection from a nickel surface which introduces new maxima between the maxima due to the nickel itself. Thus the first atoms of gas adhering to a {111} surface of clean nickel arrange themselves in a similar structure but with twice the scale factor.

Rupp³ has extended these measurements to the interaction of hydrogen with nickel, iron, copper, molybdenum and zirconium, all of which exhibit this double spacing. When exposed to hydrogen, time or brief heating effects a broadening and lessening of the maxima that correspond to the nickel and iron atoms and intensifies those due to hydrogen. This was interpreted as an opening up of the exterior of the space lattice. Thereafter nitrogen may react with hydrogen upon the surface. This is especially evident with iron surfaces which have been exposed to hydrogen.

Passive iron has also been investigated by Rupp and Schmid⁴ who find new maxima ascribable to a layer of oxygen $3.4 \text{ \AA}$.

¹ C. J. Davisson and L. H. Germer, *Phys. Rev.*, (2), 1928, **31**, 155.

² C. J. Davisson and L. H. Germer, *Phys. Rev.*, (2), 1927, **30**, 705; 1928, **31**, 155, 307, 708, 1121; L. H. Germer, *Z. Physik*, 1929, **54**, 408.

³ E. Rupp, *Z. Elektrochem.*, 1929, **35**, 586; *Ann. der Physik*, (5), 1930, **5**, 453.

⁴ E. Rupp and E. Schmid, *Naturwissenschaften*, 1930, **18**, 459.

outside the iron atoms. Surfaces contaminated with traces of grease or condensed vapours or foreign metals have been investigated by Copeland.¹

Thomson² points out that fast electrons penetrate much more deeply; that is, "a few tens of atoms" deep. He used electron beams whose energy corresponded to 30,000 volts as compared with Davisson and Germer's 300 volts. This simplifies the technique and enables a specially designed camera to be used. On the other hand, "these fast rays are uninfluenced by the thin layers of gas which are normally present on surfaces in a vacuum, or, possibly—they temporally remove the layers by bombardment". This limits the range of the method to the investigation of solid layers such as partially oxidized or otherwise chemically altered metal. For example, if the passivity of iron is due to a monomolecular or monatomic surface layer of oxygen, it is not revealed by these fast electrons. Polished or etched metals (except iron) yield no diffraction rings.

Suhrmann³ has studied the increase in photoelectric sensitivity of platinum, silver and gold whose surfaces are charged with ionized hydrogen.

The address of Mendenhall upon "Recent Developments in Photoelectricity"⁴ is so cognate to our subject that a paragraph may be quoted *verbatim*.

Early measurements of long wave limits for various metals were extremely discordant, and it only gradually came to be realized that the surface and volume conditions of the metal altered the limit and the related value of φ in a very marked way. Attempts to clean the surface produced such large changes that for a time a considerable group of experimenters held the view that for a really clean metal surface there would be no photoelectric effect whatever. It is only in the last few years that it has been possible for different observers to get concordant results. That these observers, even with their extremely pains-

¹ P. L. Copeland, *Phys. Rev.*, (2), 1930, **35**, 982.

² G. P. Thomson, *Proc. Roy. Soc. (London)*, A, 1930, **128**, 641 and 649.

³ R. Suhrmann, *Z. Elektrochem.*, 1929, **35**, 681.

⁴ C. E. Mendenhall, *Science*, 1931, **73**, 107.

taking methods, are really dealing with perfectly clean gas-free surfaces is very difficult to prove. I am inclined to think, from indirect evidence, that in many cases they are, and to hope that the values of ν_0 (or φ) now being secured can later be correlated to other fundamental properties of the metals in a systematic way." "Agreements between observations of V_c by the observer and the corresponding φ s by another must be considered accidental unless the metals have in both cases been very carefully cleaned. But no matter how contaminated the surface, if V_c and φ_1 φ_2 are measured under the same conditions, they are found to bear the theoretical relation to each other. The cleaning process, granted the metals are sufficiently free from metallic impurities, is largely concerned with the removal of gas from the surface and body of the metal, and for this only two methods have been successfully used, distillation and extreme heating in the highest possible vacuum. During the process of removing the gas, the long wave limit for a given metal may shift by as much as 1,000 Å. In some cases the shift is at first in one direction and then in the other, but such complicated effects are probably due not alone to the removal of gas but to other changes brought about simultaneously by the heat treatment. In the end (and this may be only after hundreds of hours of heating, or prolonged redistillation) surface conditions are reached which are almost completely stable as regards further treatment, and which change so slowly in the high vacua at room temperatures that accurate observations may be carried out upon them. It is such surfaces, if any, which may be said to be gas free."

"Perhaps with better controlled experiments and more elaborated theory, we can reach not only an understanding of the fundamental photoelectric process, but also, what is of equal interest and importance, a better picture of the structure of a metal surface and of the gas layers which form on it."

CHAPTER X

THE THICKNESS OF ADSORBED FILMS; AND THE AREA OF "SMOOTH" SURFACES AND POROUS BODIES

MONOMOLECULAR, MULTILAYER AND CLASSICAL THICK FILMS

It is of vital importance to the theory of sorption to know what is the possible thickness of the adsorbed layer. It is likewise both of practical and theoretical interest in many directions to know what is the real area of a supposedly smooth surface. Finally, it is a question of major importance in all branches of science to ascertain the effective range of direct molecular attraction—whether it is a microscopic distance as was the accepted belief of the older physics, or whether it is a distance of only a few Ångstrom units as is assumed by the modern electrical theory of matter in so far as it has yet been developed. It is of real interest that this is still regarded by many as an open question.

There are three points of view with regard to the thickness of the adsorbed layer. Chiefly through the influence of Langmuir it is widely held that all sorbed molecules are in contact with the molecules or atoms of the solid. Langmuir himself, in addition to many recent writers who recognize the operation of electrostatic forces only whilst stressing the predominant importance of more or less complete monomolecular layers, maintains that under highly favourable conditions, such as an environment of nearly saturated vapour, a second layer may be captured by the first and a third by the second and so on with progressively weakening force. Such built-up polymolecular layers differ in principle from the third conception, that of the older physics, still maintained in some quarters, that all the molecules coming within a

certain range of the solid are directly attracted, thus constituting a region of direct sorption whose thickness is many, or very many, times greater than a molecular diameter and which is not necessarily close packed with sorbed material.

It is the rivalry between the third or classical conception and the deceptively simple appeal of the first or monomolecular hypothesis that has lent keen interest to attempts to distinguish between them by crucial experiment. No such excitement would be aroused by a demonstration of the actual occurrence of multilayers deriving from the second hypothesis, as it would be a mere addition to the numerous kinds of monomolecular layers envisaged by Langmuir and others and lumped together indiscriminately under a common title of "monomolecular layer".

The experimental difficulty is then, first, to measure the actual amount of sorption, next to ascertain the real area of the surface involved, and then afterwards to distinguish a thick, directly attracted film from a built up structure of many layers. In no case has any one experimenter attempted all three tasks.

REVIEW OF RESULTS IN CHAPTERS VII, VIII AND IX

Summarizing the work done on glass, whether ground, leached, or fire polished, it is amply shown in Chapter VII that the real surface is usually very many times greater than the visible surface, and that it is often of altered composition. Even fire polishing is not an entirely trustworthy procedure on account of the well-known differing volatility of the constituents of glass.

As a matter of record, it must be at once conceded that the amount of sorption at high relative humidity is often vastly greater than that required to cover the apparent visible surface with a single coating of molecules. Even so, in other very numerous examples the sorption which occurs would not be sufficient to cover the visible surface.

It is of great significance that all the experiments on unspoilied fire polished surfaces of glass have shown the amount of sorption to correspond at most to a monomolecular layer.

There is one single exception; namely, the observations of Rinse¹ on the sorption of mercuric iodide. He used the McHaffie-Lenher method, but blew the glass apparatus (of high melting Jena combustion glass) through a tube containing phosphorus pentoxide, and afterwards heated it in a stream of very dry oxygen until the glass softened. He obtained two results at 300° C.; the first, a much smaller indication, immediately after the evacuation, and the larger effect after heating for two hours at 580° C. Taking the maximum value, the amount of close-packed sorbed material would be about 1,400 Å. or 667 molecules thick. His own opinion was that it was "very improbable" that the phenomenon could be regarded as adsorption, especially since with the ordinary procedure the effect nearly or quite disappeared if the glass were not heated during the preliminary evacuation. However, heating is generally a pre-requisite for the full manifestation of sorption. Possibly the glass vessel was affected by the mixture of fused potassium and sodium nitrates in which it was immersed. Certainly the effect resembles the second rather than the third conception discussed above, for if the mercuric iodide were not forming a continuous space lattice but were diminishing in concentration outwards from the glass, its thickness would be so great as to be very visible under the microscope. Taking the experiments at their face value, they indicate that the space lattice of a crystal may be so polarised through a thickness almost reaching microscopic dimensions that it may be formed even when its vapour is not quite saturated.

In the closely related work of Adhikari and Felman² upon the sorption of iodine upon liquid mercury it was shown that the sorbed iodine vapour reacted with the mercury to form

¹ J. Rinse, *J. Chem. Soc.*, **1928**, 1447. J. E. Lennard-Jones and B. M. Dent (*Trans. Farad. Soc.*, 1928, **24**, 99) show that suitably oriented dipoles may extend the space lattice of a crystal of the type of sodium chloride by an indefinite number of successive layers. O. Blüh and N. Stark (*Z. Physik*, 1927, **43**, 575) and J. H. de Boer and C. Zwikker (*Z. physik. Chem.*, Abt. B, 1929, **3**, 409) and others came to the same conclusion.

² G. Adhikari and J. Felman, *Z. physik. Chem.*, 1928, **131**, 347.

a monomolecular layer, nothing further happening until, through the chances of thermal vibration, a crystal nucleus was formed from the previously uniformly oriented iodide. Such crystal nuclei then grew rapidly, often at some distance from the position from which the iodine was first sorbed. Occasionally an iodine atom was desorbed in obvious analogy to the dissociation of mercuric iodide vapour.

Supplementing the review of the findings for glass with gases and vapours, we may add the observations of Devaux and Aubel¹ for ions from solution. A column of glass wool packed in a tube was used as the sorbing substance. The cations Ca, H, K, Na, NH₄ and quinine were sorbed reversibly by the glass, i.e. the different cations could be replaced by other cations. When the glass had not been strongly decalcified by an acid or an alkali salt, the adsorption of Ca ions was instantaneous and amounted to a single layer of Ca ions. When the glass was strongly decalcified, there was a penetration of Ca ions into the glass. This penetration corresponded to several (up to nine) layers of Ca ions and was a function of time. The glass sorbing both at its surface and in its mass therefore behaved like a porous gel. Glass microscope slides, according to Bancelin,² sorb 14×10^{-8} g. of sodium chloride, 12×10^{-8} g. of potassium chloride, and 15×10^{-8} g. of potassium bromide; fused silica likewise sorbed 13×10^{-8} g. of sodium chloride. This is enough to cover the apparent surface three close-packed ionic layers deep. Far greater sorption from aqueous solution is reported by Trouton;³ namely, chlorides, nitrates, and sulphates sufficient to cover the surface of fibres of fused silica with close-packed molecules 100 Å. deep. With dyes Bancelin⁴ found that the thickness over the apparent surface of glass threads amounted to between 10 and 40 Å.

Using a powder of fused silica which had been boiled in

¹ H. Devaux and E. Aubel, *Compt. rend.*, 1927, **184**, 601.

² J. Bancelin, *J. chim. phys.*, 1925, **22**, 534.

³ F. T. Trouton, *Report of the British Association for the Advancement of Science*, Portsmouth, 1911, p. 328.

⁴ J. Bancelin, *Compt. rend.*, 1914, **158**, 791.

nitric acid for several hours, Jones¹ was unable to detect any sorption of nitrobenzene from solution in kerosene with an interferometer that could have detected an amount sufficient to cover the apparent surface several molecules deep.

Sorption by impermeable crystals yields, according to Chapter VIII, the following somewhat inconclusive results. Fine powders and contaminated surfaces sorb large amounts of vapours at high relative humidity. Ihmori's experiments on polished quartz were too insensitive to be convincing to himself or others. Langmuir's experiments with mica gave less than enough for one complete monomolecular layer, using gases at very low pressures and vapours at somewhat higher relative pressures. Frazer's optical experiments with rock salt showed that an air film could not exceed 6 Å. and that a water film was barely detectable and therefore of monomolecular order. In no case did Durau observe sufficient sorption for a monomolecular layer on dry or moist rock salt even with sulphur dioxide, propane or nitrous oxide. Hence with impermeable surfaces, sorbed layers in general are definitely not many molecules deep and it is possible that they do not exceed one molecule in depth. There are no experiments with a surface of known area and a space lattice building substance such as mercuric iodide.

When discussing impermeable crystals, it is well to remember that it is now recognized² that perfect crystals will spontaneously develop a network of surface cracks spaced about 100 atoms apart owing to contraction due to the unbalanced forces at the surface. This must appreciably increase the area available for the sorption of small molecules. The

¹ D. C. Jones, *J. Phys. Chem.*, 1925, **29**, 372.

² See, for example, A. F. Joffé, *The Physics of Crystals* (McGraw-Hill Book Co., New York, 1928); A. Smekal, *Physik. Z.*, 1925, **26**, 707; *Z. Physik*, 1927, **45**, 869; F. Zwicky, *Proc. Nat. Acad. Sci.*, 1929, **15**, 253. J. E. Lennard-Jones and B. M. Dent (*Proc. Roy. Soc. (London)*, A, 1928, **121**, 247) have shown that the outermost layer of atoms of the (100) face of crystals of the type of sodium chloride is 5 per cent closer to the underlying layer and is contracted laterally by 5 per cent as compared with the normal spacing within the body of the crystal.

remarkable experiments of Griffith ¹ with fibres of glass and silica show that even a "virgin fire polished" surface of fused silica does not remain intact if exposed even for a few hours.

Sallinger ² found that the sorption of the hydroxides of the alkalis and alkaline earths from aqueous solution by powdered quartz corresponded to a monomolecular layer or less if the space lattice dimensions were taken for the cation, and to many layers (four- to fifteen-fold) if Remy's values for fully hydrated cations were employed. Thoulet ³ found that powdered quartz sorbed 1.8×10^{-6} g. of barium chloride per square centimetre, which would be several dozen ionic layers deep if referred to the surface estimated under the microscope. Estimating the surface by counting colloidal particles under the ultramicroscope, Gustaver ⁴ calculated that the amount of sodium chloride taken up by Oden's sulphur was of the order of a monomolecular layer, and, similarly with Chakravarti and Dhar's ⁵ colloidal barium sulphate, the sorption of various electrolytes was insufficient to cover the surface.

Fajans and Frankenburg ⁶ measured the sorption of silver nitrate by colloidal particles of silver bromide which they counted just before coagulation and found the sorption of silver ions was only a fraction of that required for a monomolecular layer.

As regards sorption by liquid metals (mercury), the writer has given reasons for rejecting the few results of the optical method, which, however, has not been used with vapours. The direct measurements of Oliphant and Burdon for sorption of carbon dioxide and of Volmer and Mahnert for benzophenone lead to values not exceeding that for a monomolecular film. So do Iredale's calculations from the Gibbs' theorem. Euler

¹ A. A. Griffith, *Trans. Roy. Soc. (London)*, A, 1920, **221**, 163.

² H. Sallinger, *Kolloidchem. Beihefte*, 1927, **25**, 373.

³ J. Thoulet, *Compt. rend.*, 1885, **100**, 1002.

⁴ B. Gustaver, *Kolloidchem. Beihefte*, 1922, **15**, 185.

⁵ M. N. Chakravarti and N. R. Dhar, *Kolloid-Z.*, 1928, **45**, 17.

⁶ K. Fajans and W. Frankenburg, *Z. physik. Chem.*, 1923, **105**,

and Zimmerlund¹ found that a mercury surface sorbs only a very small fraction of the amount of mercurous chloride required for a monomolecular layer.

With ordinary platinum surfaces Warburg and Ihmori could not measure the sorption of water vapour, but Strömberg obtained thick films such as 42 Å. at half saturation, rising almost asymptotically to 380 Å. for saturated vapour. This is in spite of Langmuir's opinion,² "we may safely assume that water vapour would not penetrate at all into a metal, so that a *clean* metal surface should never take up more moisture than enough to form a layer one molecule deep". The question arises as to whether this surface was sufficiently porous to permit of capillary condensation (compare Chapter IX, fig. 90). Langmuir's experiments with platinum, Durau's with silver, and Kälberer and Mark's with aluminium clearly corresponded to monomolecular films or less. Similarly, Langmuir's studies of electronic emission from thoriated tungsten indicate that the surface film of thorium is not more than one atom thick.³

Polished platinum and amalgamated platinum sorb thick films of water or benzene from nearly saturated vapour. On the other hand, amalgamated silver does not sorb more than one layer of water molecules or other polar substances.

It is the writer's opinion that, in view of the great uncertainties attaching to the nature and extent of ordinary metallic surfaces, the crucial experiments will have to be carried out upon liquid metallic surfaces. To carry conviction to all concerned, it must be shown, either that monomolecular layers are not exceeded by even the most likely substances at high relative or absolute pressures or, on the contrary, that thicker layers do occur with substances free from sus-

¹ H. von Euler and G. Zimmerlund, *Arkiv Kemi, Mineral. Geol.*, 1921, **8**, No. 14; H. von Euler, *Z. Elektrochem.*, 1922, **28**, 4.

² I. Langmuir, *J. Am. Chem. Soc.*, 1916, **38**, 2284.

³ I. Langmuir, *Phys. Rev.*, (2), 1922, **20**, 107; 1923, **22**, 357, *J. Am. Chem. Soc.*, 1916, **38**, 2281, footnote 1. For much further evidence as to the monatomic nature of coatings of metals and oxides on metal filaments, see S. Dushman, *Reviews of Modern Physics*, 1930, **2**, 381.

picion of building up space lattices or a scum of reaction products.

Supplementing this summary of the work on metals, reference should be made to the work of Euler, Hedelius and Zimmerlund¹ who studied sorption from solutions by exceedingly fine silver powder, gold powder and very thin gold foil.

The number of gram mols of silver nitrate sorbed by one apparent square metre of silver powder (estimated by observation under the microscope) was 3.5×10^{-4} ; that of potassium chloride, 5×10^{-4} . Using gold foil (90.8 per cent gold; 8.5 per cent silver; some lead), the amounts sorbed per square metre of apparent surface were 7×10^{-5} mols of silver nitrate, 2×10^{-5} mols of potassium chloride, 7×10^{-5} equivalents of silver sulphate, corresponding to 4×10^{19} atoms of silver or 1.2×10^{19} of potassium or chlorine per square metre; whereas a monatomic layer of close-packed silver atoms could not accommodate more than about 2×10^{19} of silver or 1×10^{19} of chlorine. In other words, the apparent surface is covered with two layers of molecules of silver nitrate laid vertically end to end (four ions deep) or with 1.2 molecular or 2.4 ionic layers of potassium chloride. Nearly equivalent amounts of cation and of anion were sorbed in each case.

In a later paper Euler and Rudberg² found that the results with potassium chloride were due to superficial oxide and that clean surfaces sorbed no potassium chloride, ammonium thiocyanate, sulphuric acid or sodium sulphate. Using sheet gold, they obtained 5×10^{-5} mols of silver nitrate per square metre, and with sheet silver up to 9×10^{-5} mols per square metre. In the latter case the sorption was the same when the silver surface was given a high polish and when it was etched with 4 N nitric acid. The sheet gold had been cleaned

¹ H. von Euler and A. H. Hedelius, *Arkiv Kemi, Mineral. Geol.*, 1920, **7**, No. 31; H. von Euler, *Z. Elektrochem.*, 1922, **28**, 2; H. von Euler and G. Zimmerlund, *Arkiv Kemi, Mineral. Geol.*, 1921, **8**, No. 14.

² H. von Euler and E. G. Rudberg, *Z. Elektrochem.*, 1922, **28**, 446.

with the same reagent. The same amount of silver nitrate was sorbed from solution in 96 per cent alcohol.

These results, which have been misquoted or misunderstood by some other authors, correspond to 3×10^{19} atoms of silver and 5.4×10^{19} atoms of silver per square metre, whereas a monatomic layer of close-packed silver atoms could not contain more than 2×10^{19} anhydrous silver atoms. Hence the apparent surface was covered with 1.5 to 2.7 molecular layers of silver nitrate; that is, 3 to 5.4 ionic layers deep. Euler and Rudberg prefer to take this as a measure of the degree by which the real surface exceeds the apparent surface.

METHODS OF ESTIMATING AREAS

In general, the amount of a solid exposed to the action of a gas or liquid is much greater than the visible apparent surface. This has been demonstrated in many ways; and the extent to which they may be utilized to measure the area available for sorption will now be discussed.

(a) *Sorption of radioactive elements*

In experiments carried out with finely divided lead sulphate, Paneth¹ employed a solution containing an isotope of lead, namely, thorium B, as "radioactive indicator". During adsorption the isotope replaces some of the lead atoms on the surface of the lead sulphate, these lead atoms entering the solution until the ratio of the quantity on the surface to that in solution is the same for the lead atoms and for its isotope. Reversible equilibrium is so quickly established that it seemed a safe conclusion that the rearrangement extended only to the exposed atoms on the surface of the crystal, although it would include cracks and crevices. The distribution of the isotope is found by means of an electroscope,

¹ F. Paneth, *Z. Elektrochem.*, 1922, **28**, 113; F. Paneth and W. Vorwerk, *Z. physik. Chem.*, 1922, **101**, 445, 480. O. Hahn and L. Imre (*Z. physik. Chem.*, Abt. A, 1929, **144**, 161) have greatly extended the study of the sorption of radioactive elements by crystalline precipitates under various conditions.

and the quantity of lead in solution is determined analytically. Hence the exposed surface of the powder of lead sulphate becomes known. It was found to be twice that estimated from microscopic observation. Paneth and Thimann¹ extended the measurements to other well-formed crystalline lead salts and to the isomorphous sulphates of barium, strontium and calcium, using thorium B and thorium X, with similar results, sometimes finding the areas given by this method to exceed the visible surface by only 20 per cent.

(b) *Sorption of dyes*²

Turning to account the knowledge of the surface of crystals of lead sulphate as measured by the radioactive method, Paneth and Vorwerk used the same preparation of lead sulphate for the sorption of the dye Ponceau Red 2R. The maximum amount sorbed would cover 31 per cent of the surface if the molecules of the dye were close-packed cubes, but it would cover the surface with a monomolecular layer if the molecules lay flat upon the surface so that one molecule of dye covered eleven molecules of lead sulphate. Paneth and Thimann also used methylene blue, naphthol yellow and methyl green, sodium brucine sulphonate and acetone with lead sulphide, sulphate, phosphate and bismuth trisulphide. None exceeded a monomolecular layer and many were less. Methylene blue HB and acetone came nearest to a complete monomolecular film, whereas methylene blue B extra covered only 68 per cent of the surface.

Attempting still further to exploit the results based upon the radioactive method, Paneth and Radu³ measured the sorption by powdered diamond of sufficient coarseness that

¹ F. Paneth and W. Thimann, *Ber.*, 1924, **57B**, 1215.

² It was first noticed by R. Marc (*Z. physik. Chem.*, 1910, **73**, 685; 1911, **75**, 710; 1913, **81**, 641) that a number of dyes exhibited a saturation value when sorbed by crystals and that the ratio between the amounts of different dyes sorbed at saturation was independent of the nature of the crystal. It is instructive to read his discussion and note the difficulties due to the lack of the conception of the monomolecular layer of Haber and Langmuir.

³ F. Paneth and A. Radu, *Ber.*, 1924, **57B**, 1221.

its area could be estimated under the microscope, using "methylene blue" and methyl green. When they assumed that 1 milligram of "methylene blue" covered 1 square metre (10,000 sq. cm.), it covered between 50-100 per cent of the microscopically estimated surface and methyl green covered about three-quarters as much. This rule, "one milligram methylene blue indicates one square metre of surface",¹ has since been often employed by other workers. Paneth and Thimann's original data are reproduced in table 42. Of the three dyes, methylene blue always gave the highest result. The several fold higher results with acetone are ascribed to its better penetration into the porous charcoal.

TABLE 42

Specific Surface of Various Charcoals by Paneth and Radu's Method of Dyes

Substance Sorbed	Mol. Wt.	Carbo Animalis pur. (Merck)		Lime Charcoal (Kahlbaum)		Bone Charcoal (Kahlbaum)		Activated Sugar Charcoal	
		Molecules $\times 10^{-20}$	Sq. M.	Molecules $\times 10^{-20}$	Sq. M.	Molecules $\times 10^{-20}$	Sq. M.	Molecules $\times 10^{-20}$	Sq. M.
Methylene blue B extra	338	4.14	220	1.89	101	3.17	168	0.47	24.8
Methyl green	595	2.56	190	1.26	95	1.54	114	0.26	19.2
Ponceau 2R	480	1.90	119	0.985	61	1.65	103	0	0
Pb(NO ₃) ₂	331	6.07	123	2.16	46.2	4.50	97.8	0.61	13.2
Acetone	58	18.5	452	11.0	268	14.7	359	2.29	55.9

The values given by methylene blue are thus only a useful first approximation. A further application and limitation of

¹ It is of interest to note that 1.5 mg. of nonylic acid, in close-packed film, cover one square metre of water.

the method are evident from Paneth and Radu's values for artificial silks quoted in table 43.

TABLE 43

Specific Surface (in Square Metres) of Artificial Silks by Paneth and Radu's Method of Dyes

Sorbing substance	Nitro silk	Cuproammonium silk	Acetate silk
Microscopic estimation	12	15	30
Methylene blue B extra	1,280	456	28

The first two silks are coloured uniformly through and through, but the acetate silk is only superficially coloured. The latter is therefore serving as an ultrafilter, whereas the first two are freely porous.¹

Durau² was on far less certain ground than Paneth when he compared the sorption of dye by silver filings with that sorbed by silver rods of supposedly known dimensions. The rods sorbed 2.1 mg. of ethyl violet on one square metre of apparent surface of silver wire, but the real surface would exceed this. This, however, merely strengthens his conclusion that the sorption he observed was much less than monomolecular. Again, van der Grinten's³ observations with glass would require the molecules of crystal violet to be cubes if this apparent surface were to be taken as the real surface. Hence the real surface accessible to the dye was three or four times greater.

That the method of dyes has to be regarded with great reserve was shown by Bancroft and Barnett.⁴ They showed that with one concentration of "methylene blue", the sorption by lead sulphate varied seven-fold over the range of *pH* studied, being at a maximum between *pH* 6.5 and 7.1. When the concentration was varied, the maximum observed again depended upon the value of the *pH*. They conclude :

¹ This points to the obvious method of making the dyeing properties of acetate silk resemble the others.

² F. Durau, *Z. Physik*, 1926, **37**, 419.

³ K. van der Grinten, *J. chim. phys.*, 1926, **23**, 209.

⁴ W. D. Bancroft and C. E. Barnett, *Colloid Symposium Monograph* (Toronto, 1928), 1928, **6**, 73.

"It is not possible at present to use the maximum adsorption of a dye by crystals as a measure of the total surface." Hence Paneth's standard result with lead sulphate is to be regarded as a coincidence.

The extent to which mere sorption of a dye, even "methylene blue", may be misleading is illustrated by the experiments of Bancelin.¹ He found that one square metre of liquid mercury sorbed 0.13 mg. of "methylene blue", thus underestimating it by eight-fold. Other dyes gave similar or varying results.

(c) *Rate of chemical attack*

Wolff² attempted to define the area of glass by the rate at which it dissolved in sodium hydroxide and sodium carbonate under carefully standardized conditions. Not all powdered glass yields consistent results. He was satisfied with the comparison made with one kind of window glass (experiments were also carried out with three kinds of Jena glass and photographic plates), taking the apparent surface of the glass sheets as a standard for deducing the surface of a fine powder of the same glass.

This method was linked to the method of dyeing by Schmidt and Durau.³ They first compared by Wolff's method the apparent surfaces of window glass with a specimen of the same glass in powdered form. Different specimens of glass powdered to pass through the same sieve gave different results. They then measured the sorption of methyl violet and diamond fuchsine by the glass powder. The amount of methyl violet sorbed was sufficient to cover the apparent

¹ J. Bancelin, *J. chim. phys.*, 1925, **22**, 522.

² H. Wolff, *Z. angew. Chem.*, 1922, **35**, 138. G. Martin and collaborators (*Trans. Ceramic Soc. (England)*, 1924, **23**, 61; 1925-26, **25**, 51, 63) used hydrofluoric acid with sand and quartz; K. Kasai (*Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1930, **13**, 147) used it with glass; G. Gehlhoff and R. Schmidt (*Spechsaal*, 1927, **60**, 336) studied glass plates in soda solution and in water at 100° C.; P. Tietze (*Spechsaal*, 1927, **60**, 813) determined by titration the amount of glass dissolving in water.

³ G. C. Schmidt and F. Durau, *Z. physik. Chem.*, 1924, **108**, 128.
S.G.V. Z

surface with a double layer of molecules if the latter were assumed to be anhydrous cubes. If they lay flat upon the surface, the number of molecular layers would be many times greater. They would have to be elongated and close packed end on to the surface to put them into one layer. Exactly the same result was obtained with diamond fuchsine.¹ The methods of chemical attack and of dyeing were shown to agree with each other but both are dependent upon the assumption that the visible surface of a glass plate is its real surface—an assumption which is always an underestimate, sometimes even to the extent of one or more decimals.

Schelte² extended Schmidt and Durau's measurements, using lead glass 19523 of Schott and Genossen obtained from two different melts. The two differed only slightly in their rate of chemical attack. He also used some of the original window glass. The results obtained by Schelte with various dyes on powdered glass which had been cleaned with hydrochloric acid (not used with the sheet glass) are displayed in table 44.

TABLE 44

Number of Layers of Cube-shaped Molecules corresponding to the Sorption of various Dyes by the same Glass.

	Methyl violet	Ethyl violet	Diamond fuchsine	" Methylene blue "
Window glass . . .	1.97	1.65	1.98	1.36
Lead glass . . .	1.92	1.40	0.75	0.80

It is evident that the various dyes do not give more than an approximate comparison of the size of glass surfaces. The absolute values will be still more in error.

The same lead glass was employed by Isselstein³ and, after

¹ N. S. Sheinker (*J. Russ. Phys.-Chem. Soc.*, 1929, **61**, 413; through *Chemical Abstracts*, 1930, **24**, 281) obtained the same result as Schmidt and Durau with methyl violet BB, diamond fuchsine and brilliant safranine, but using the visible surface of glass wool as the basis for calculation. He adds that no increase (no further increase?) is caused by treatment with water and acids.

² F. Schelte, *Z. physik. Chem.*, 1925, **114**, 394.

³ M. T. Isselstein, *Physik. Z.*, 1928, **29**, 873.

thorough washing with hydrochloric acid, its surface was determined with ethyl violet and diamond fuchsine, using Schelte's values per square centimetre; and upon this basis the sorption of carbon disulphide, pentane and methyl chloride corresponded to layers as much as 35 molecules deep.

In all this work it is evident that the area of the glass surface was underestimated; first, because it was assumed that the visible surface of the original glass was identical with the true surface; second, because the real area of the powder was greatly enhanced by treatment with acid, although this was not allowed for in the calculation; and third, because, as in Paneth and Radu's experiments, these small molecules would penetrate the silica gel more extensively than the large molecules of dye. There is therefore no evidence from this work that a monomolecular layer is ever exceeded.

One apparent square metre of glass in the form of rods or plates was found by Bancelin¹ to sorb over 10 mg. of crystal violet, "methylene blue", or fuchsine. This is enough to cover the apparent surface with nearly 10 molecular layers if the molecules are assumed to be cubes, less if the molecules are vertical and elongated, and many more if they lie flat.

An exceptionally elaborate and careful study has been made by Kasai² of the estimation of the surface of powders by various geometrical methods and by comparison with the diameters inferred from Stoke's law. He used powdered window glass separated into four grades by winnowing and determined its surface according to the method of chemical attack and by the method of Traube and Nishizawa.³ The result was to show that the real surface exceeded that estimated geometrically several fold, depending upon the particular evaluation adopted, although some of these modes of calculation agreed fairly well with the method of elutriation using Stoke's law.

¹ J. Bancelin, *J. chim. phys.*, 1925, **22**, 518.

² K. Kasai, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), 1930, **13**, 135; where many interesting references to related work are to be found. See also F. V. von Hahn, *Dispersoidanalyse, die Methoden der Teilchengrossenbestimmung und ihre theoretischen Grundlagen*, Theodor Steinkopff, Dresden and Leipzig, 1928.

³ J. Traube and K. Nishizawa, *Kolloid Z.*, 1923, **32**, 392.

Traube and Nishizawa¹ utilized caprylic acid to determine how much powder or surface had to be added for complete sorption, as shown by surface tension approaching that of water. Surface tension was observed with the stalagmometer (Kasai observed the rise in a capillary tube).

Silver bromide sorbs orthochrome T-bromide at a *pH* value of 5.5 to the extent of one molecule of dye for two ions of the exposed lattice surface, as was observed by Sheppard.² This, of course, is much more than a monomolecular layer.

(d) *Polarization during electrolysis*

The only method to be placed beside that of Paneth, described under heading (a) above, is that developed by Bowden, Rideal, McAulay, Mellor and O'Connor³ to determine the area accessible for adsorption.

A metal is made the cathode in a dilute acid and the quantity of electricity, ΔQ , which must be passed across the interface to cause a given change in the electrode potential is measured. The quantities involved are far less than would suffice to produce a monomolecular layer of hydrogen atoms. For example, 6×10^{-7} coulombs per square centimetre⁴ cause a change of 100 millivolts in the electrode potential at a mercury surface, corresponding to 1/3000 of an atomic layer of hydrogen. The effect is in linear proportion to the quantity of electricity, ΔQ .

The quantity ΔQ is found to be independent of the chemical nature of the metal as shown by a study of mercury, liquid amalgams, platinized mercury, liquefied Wood's alloy and liquid gallium. It therefore appears to measure the accessible area of the metal. This is greatly increased when the liquid

¹ J. Traube and K. Nishizawa, *Kolloid Z.*, 1923, **32**, 392.

² S. E. Sheppard, *Nature*, 1926, **118**, 914.

³ F. P. Bowden and E. K. Rideal, *Proc. Roy. Soc. (London)*, A, 1928, **120**, 59, 80; A. L. McAulay and D. P. Mellor, *Nature*, 1928, **122**, 170; F. P. Bowden, *Nature*, 1928, **122**, 647; *Proc. Roy. Soc. (London)*, A, 1929, **125**, 446; F. P. Bowden and E. A. O'Connor, *Proc. Roy. Soc. (London)*, A, 1930, **128**, 317.

⁴ The corresponding oxygen overpotential is 110×10^{-7} coulombs per 100 millivolts.

solidifies and is still further magnified by abrasion or chemical attack. The magnitude of this increase is well displayed in table 45 which gives the ratio between accessible area of the solid and that of a liquid of equal apparent surface.

TABLE 45

*The Ratio between True * Surface and the Apparent Surface or that of a Liquid as found by the Method of Electrolytic Polarization.*

Surface	Ratio
Platinum, bright foil	2.2
Platinum, bright foil, cleaned in acid and heated in a flame	3.3
Platinum, platinized	1,830
Gallium, solidifying undisturbed	1.7
Nickel, polished, new	75
Nickel, polished, old	9.7
Nickel, activated by alternate oxidation and reduction, new	46
Nickel, activated by alternate oxidation and reduction, old	29
Nickel, activated, then annealed, new	10.8
Nickel, activated, then annealed, old	7.7
Nickel, repolished and electroplated, new	12
Nickel, repolished and electroplated, old	9.5
Nickel, rolled, new	5.8
Nickel, rolled, old	3.5
Wood's metal, solidifying undisturbed	1.4
Wood's metal, sandpapered	6.3
Wood's metal, corroded by etching with nitric acid	800-1,000
Silver, freshly etched with dilute nitric acid	51
Silver, etched with dilute nitric acid, after 20 hours	37
Silver, finely sandpapered	16
Silver, amalgamated, after 1 hour	1.2
Silver, amalgamated, after 20 hours	1.3
Silver, amalgamated, after 150 hours	1.8
Arc carbon rod	328-366†

* The true surface is here defined as that which is accessible to hydrogen atoms. Obviously, as it has been pointed out by Bowden, if a much smaller or much larger object than the hydrogen atom were used for measurement, the area might be given a different value.

† Using the "methylene blue" rule, this carbon had an area of 100 to 165 sq. cm. per apparent square centimetre, as measured by sorption at 1 and 4 days, respectively.

Especially interesting are the varying data for the same piece of metal as it is put through the consecutive treatments described in the table. The results in table 45 are of general interest and significance even although they are essentially confined to metallic surfaces. They required elaborate appar-

atus in view of the small quantities of electricity and short periods of time involved in the measurement. It consisted essentially of an Einthoven string galvanometer with a moving film camera to photograph its indications. The total quantity of electricity required to change the hydrogen electrode potential on platinum to an oxygen potential is equal to that necessary to remove one hydrogen atom from each atom of platinum on the accessible surface and replace it by an oxygen atom. Twice as much would be required for close packed monatomic layers of gas.

(e) *Interference colours*

A crude method for estimating surface area of metals has been introduced by Constable.¹ Having shown that the colour of the oxide film formed on metals, such as nickel, copper and iron, is due to interference and is consequently determined uniquely by its thickness, he calculates the volume of a film from its weight and the density of the oxide, and combines this with its thickness, as determined by its colour, to estimate the specific area of the surface. Bowden and O'Connor² reiterate the criticism that, since it necessarily involves the destruction of the metal surface to a depth of some thousand atoms, and since it does not detect irregularities of less than 1,000 Å., it cannot give information upon the area and configuration of the surface atoms.

The nature of a partially oxidized metallic surface is vividly portrayed in fig. 109³ which represents the findings of Evans and his collaborators.⁴ It shows the composite nature of the

¹ F. H. Constable, *Nature*, 1926, **118**, 730; 1927, **119**, 349; 1927, **120**, 769; *J. Chem. Soc.*, **1927**, 1578; *Proc. Roy. Soc. (London)*, A, 1927, **115**, 570.

² F. P. Bowden and E. A. O'Connor, *Proc. Roy. Soc. (London)*, A, 1930, **128**, 318.

³ U. R. Evans and J. Stockdale, *J. Chem. Soc.*, **1929**, 2651, fig. 1.

⁴ U. R. Evans, *J. Soc. Chem. Ind.*, 1925, **44**, 163T; *J. Chem. Soc.*, **1927**, 1022; **1929**, 92; *Nature*, 1927, **120**, 584; 1929, **123**, 16; U. R. Evans and J. Stockdale, *J. Chem. Soc.*, **1929**, 2651; U. R. Evans and L. C. Bannister, *Proc. Roy. Soc. (London)*, A, 1929, **125**, 370.

surface region and is also a reminder of the occurrence of numerous crevices in a metallic surface.

Constable's method may even indicate a specific surface less than the visible apparent surface.¹ The growth of films upon metals and the various methods of estimating their thickness are referred to or discussed by Evans and Bannister.²

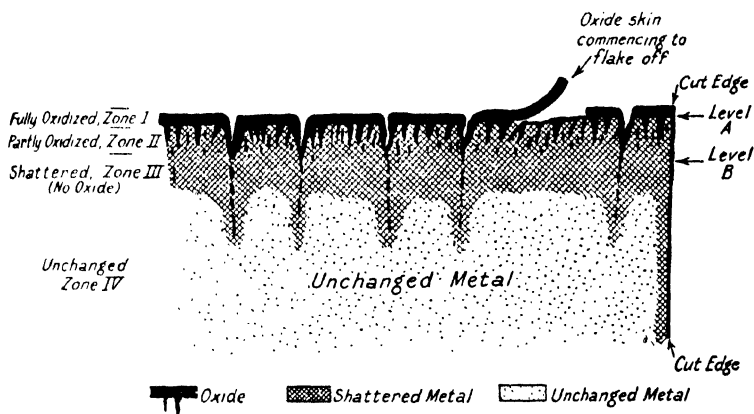


Fig. 109.—Cross Section through a Sheet of superficially Oxidized Metal.

(f) *Rate of vaporization*

Wilkins³ points out that if the vapour pressure and likewise the rate of vaporization of the solid be measured, comparison of the latter with the value predicted from the kinetic theory of gases (Knudsen equation) should give the ratio between real and apparent surface.

(g) *Assumption that the sorption of water measures the total area of the pores in charcoal*

The assumption that water is neither adsorbed nor absorbed by charcoal but is merely condensed as liquid in the capillary

¹ F. J. Wilkins, *J. Chem. Soc.*, **1930**, 1304.

² U. R. Evans and L. C. Bannister, *Proc. Roy. Soc. (London)*, A, **1929**, **125**, 370.

³ F. J. Wilkins, *Nature*, 1930, **125**, 236.

pores was based upon the fact that the sorption isotherm for water with charcoal commonly departs from the usual form in that the sorption sets in at moderately high relative humidity and then rapidly rises to fairly high values. Using the formulæ discussed in Chapter XVI, each relative pressure would correspond to a particular diameter of pore, and the amount of sorption occurring at that relative pressure would give the total cross section of all pores of that size. By a process of summation, it is evident that the total internal surface of an equivalent set of round pores may be calculated. A number of investigators,¹ mostly connected with the American Chemical Warfare Service, has assumed that this is the area upon which the adsorption of other gases and vapours takes place. It is upon this basis that the sorption of gases is held by them to be less than monomolecular. Since the pores are of molecular dimensions, the application of the capillary formula is of doubtful validity. Furthermore, Porter's² demonstration of the expansion of active charcoal when exposed to unsaturated water vapour disproves the fundamental assumption.

(h) *Heat of wetting*

Parks³ and Nutting⁴ compared the areas of surfaces of sand and precipitated silica and even glass wool by placing them proportional to the respective heats of wetting. Parks found the latter to be for water 0.00105 cal. per sq. cm., for all three after heating and evacuation. The apparent surface was estimated by observation under the microscope.

As distinguished from these relative comparisons the method of Bartell and Fu⁵ appears to yield an absolute

¹ For example, H. H. Lowry and G. A. Hulett, *J. Am. Chem. Soc.*, 1920, **42**, 1393; H. H. Lowry, *J. Am. Chem. Soc.*, 1924, **46**, 836; *J. Phys. Chem.*, 1930, **34**, 63.

² See Chapter IV, page 148.

³ G. J. Parks, *Phil. Mag.*, (6), 1902, **4**, 240; 1903, **5**, 517.

⁴ P. G. Nutting, *J. Phys. Chem.*, 1927, **31**, 531.

⁵ F. E. Bartell and Y. Fu, *Colloid Symposium Annual* (Johns Hopkins, 1929), 1930, **7**, 138.

measurement of the surface of certain powdered solids. Their equation is

$$a = \frac{-Q}{A - KT \frac{ds}{dT}}$$

where a is the area in square centimetres, $-Q$ is the heat of wetting directly determined, T is the absolute temperature, S the surface tension of the liquid against air, A is the difference between surface tension of the solid against air and the surface tension of the interface solid-liquid, and $K = A/S$. The surface tensions of the solid are unknown, but the difference in surface tension of the solid against air and against the liquid has been arrived at by the ingenious method of Bartell and Osterhof.¹ The latter employ a rod of compressed carbon or silica powder with a series of liquids, singly and in immiscible pairs. They determine the pressure with which a completely wetting liquid with zero contact angle displaces air from the porous rod, then the corresponding pressure for an imperfectly wetting liquid with finite contact angle, and finally the pressure with which one liquid displaces the other from the same rod. This yields the value of the "adhesion tension" A and, hence, also K .

With a particular specimen of activated sugar charcoal the area of one kilogram was found to be 6.2, 6.3, 6.1, 6.8, 6.3, mean 6.3, in each case $\times 10^5$, square metres, using benzene, chloroform, carbon disulphide, ethyl carbonate and carbon tetrachloride, respectively. For a kilogram of silica gel the area in square metres $\times 10^{-5}$ was found to be 5.0, 4.3, 4.5, 4.5, 4.3, mean 4.5, using water, benzene, chloroform, nitrobenzene and carbon tetrachloride, respectively. It will be seen that the results for a given solid are consistent when different liquids are used, although these must be inert and not like alcohol with carbon. With a silica gel containing 4 per cent of water the area found with four liquids was 7.3×10^5 square metres per kilogram.

¹ F. E. Bartell and H. J. Osterhof, *Colloid Symposium Monograph* (Michigan, 1927), 1928, 5, 123.

"This method of determining surface area does not depend on the measurement of adsorption from solution; it is therefore free from those uncertainties which arise from the use of doubtful assumptions concerning the shape and dimension of the adsorbed molecules, and the unknown thickness of the adsorbed layer, which assumptions are unavoidable in the adsorption as used at present. This method can be applied to those solids for which there is no solvent, because the method does not depend on solubility determinations."

The assumption is made that the rod prepared from compressed powder is of rigid dimensions with pores whose size remains constant during the treatment. This is not quite true as is clearly shown in Chapter XIII.

The most serious question is as to whether the conceptions of definite surface tensions and contact angles are legitimately applicable to surfaces and pores of molecular dimensions, such as are concerned in persorption by charcoal and silica (see Chapters IV to VI). There is always the further question as to whether the results with water would be affected by more drastic evacuation. However, if we accept Bartell and Fu's values, we may suggest the following significant calculation. If for a typical sorption of a substance of molecular weight of say, 60, the value of the sorption $x/m = 0.3$, the sorption per square centimetre would be 5×10^{14} molecules, which would almost constitute one monomolecular layer. The results of Bartell and Fu's method would be a proof that persorption by activated charcoal or by silica gel is essentially monomolecular.

In contrast to this, Iliin's ¹ mathematical formulation of the heat of sorption regarded as adsorption potential, ascribing adsorption entirely to electrical action, yields a surface ten times smaller and hence ten times as much sorption per square centimetre. On the other hand, the equations of Williams,²

¹ B. Iliin, *Z. physik. Chem.*, 1925, **116**, 431.

² A. M. Williams, *Proc. Roy. Soc. (London)*, A, 1919, **96**, 310. See also A. Eucken, *Vorh. deut. physik. Ges.*, 1914, **16**, 345; H. Zeise, *Z. physik. Chem.*, 1928, **136**, 413; their equations indicate that a monomolecular layer is not exceeded either above or below the critical temperature of the gas.

based directly upon well-known theorems of the kinetic theory of gases (used also by Debye and Jaquet ¹), when applied to the same experimental data of Titoff as those discussed by Iliin, indicate that the sorbed layer is not more than 4 Å. deep; that is, only thick enough for one layer of molecules. Finally, experiments of McBain and Britton ² appear to afford a direct proof that persorption in charcoal is essentially monomolecular (see Chapter IV, page 108, and Chapter XVII, page 459).

(i) *Bends in curves for porous bodies*

Keyes, Marshall and Bramston-Cook ³ interpret changes in direction in the curves for heats of sorption by charcoal with increasing amounts sorbed as indicating the existence of successive layers of adsorption upon an original primary layer. This point of view, together with the quantities sorbed, leads to the conclusion that the specific surface was between 0.03 and 0.06×10^5 square metres per kilogram. On the other hand, McKie, ⁴ who has likewise studied the heat of sorption of oxygen by charcoal, is of the opinion that these experimenters did not obtain sufficient sorption altogether to complete even a monomolecular layer. Ward and Rideal ⁵ likewise point out that the highest sorptions in question would suffice to cover only one-fiftieth of the area of the charcoal accessible to methylene blue.

Garner, McKie, Knight and Kingman ⁶ utilize changes in direction of the anomalous sorption isotherms, which they obtained with normal aliphatic alcohols in aqueous solution

¹ E. Jaquet, *Fortschritte Chem., Physik, physik. Chem.*, 1925, **18**, Heft 7, p. 6.

² J. W. McBain and G. T. Britton, *J. Am. Chem. Soc.*, 1930, **52**, 2198.

³ F. G. Keyes and M. J. Marshall, *J. Am. Chem. Soc.*, 1927, **49**, 156; M. J. Marshall and H. E. Bramston-Cook, *J. Am. Chem. Soc.*, 1929, **51**, 2025.

⁴ D. McKie, *J. Chem. Soc.*, **1928**, 2888.

⁵ A. F. H. Ward and E. K. Rideal, *J. Chem. Soc.*, **1927**, 3127.

⁶ W. E. Garner, *Trans. Farad. Soc.*, 1926, **22**, 459; W. E. Garner, D. McKie and B. C. J. G. Knight, *J. Phys. Chem.*, 1927, **31**, 641; W. E. Garner and F. E. T. Kingman, *Trans. Farad. Soc.*, 1929, **25**, 24.

with carbon, to indicate completion of monomolecular layers. These breaks were observed in low dilutions, using a surface tension method to measure concentration. However, using the interferometer instead, normal smooth isotherms were obtained, which led Garner and Kingman "to mistrust" the previous results.

THICKNESS OF FILMS AND RANGE OF MOLECULAR ATTRACTION

(a) *Insoluble films*

Films of insoluble substances on water are usually monomolecular. In exceptional cases where this is exceeded it is due to compounds having been purposely selected with a view to capturing successive layers. The same comment would appear to apply to the layers of soap or fatty acids upon base metals as examined by means of X-rays by Trillat.¹ Perrin² and others have observed the building up of thick films from successive layers in close analogy to the formation of lamellar crystals. It is evident that the operative mechanism is here exerted between molecules in direct contact, and yields no information about a possibly wider range of molecular attraction.

(b) *Liquid films*

Here again, a large and important subject may be briefly dismissed, because its interest lies outside the scope of the present book. Liquids consist in effect of close-packed molecules. Hence, no matter how deep the layer of liquid through which the influence of the boundary may be felt, the results may be interpreted as an influence from molecule to molecule, as in the hypothesis of Hardy³ and of McBain,⁴ and afford no conclusive evidence for or against the existence of the wider range of molecular attraction envisaged by classical physics.

¹ J. J. Trillat, *Compt. rend.*, 1925, **180**, 1838.

² J. Perrin, *Kolloid-Z.*, 1930, **51**, 2.

³ W. B. Hardy, *J. Gen. Physiol.*, 1927, **8**, 641.

⁴ J. W. McBain, *Nature*, 1927, **120**, 362; J. W. McBain and G. P. Davies, *J. Am. Chem. Soc.*, 1927, **49**, 2230; J. W. McBain and R. DuBois, *J. Am. Chem. Soc.*, 1929, **51**, 3534.

Some of the investigations of this fascinating and important problem may be listed as follows: Quincke¹ studied the thickness of the water film between lenses of glass by observing the boundary of total reflection; and determined² how thick a (colloidal) film of silver, silver sulphide, silver iodide, or collodion on glass has to be before the contact angle with the liquid becomes constant (500 Å.).

Schleiermacher³ studied the specific gravity of glass, platinum black, mica, silver on glass, copper, platinum and brass before and after fine subdivision, hoping thereby to detect any difference in density in the water in immediate contact with the solid from that of water in bulk, but finding it not greater than the experimental error which was 0.1 g. per 10,000 sq. cm. He even obtained an apparently negative value when comparing glass with the same glass blown into thinnest films.

Meyer,⁴ Williams,⁵ Weber and Lewin⁶ and others have attempted to evaluate the thickness of a film of liquid adhering to an immersed solid, finding it microscopic, whereas Goucher and Ward⁷ found it negligible.

Reichinstein's "displacement principle" (compare Chapter IV, page 166) leads to the inference that the thickness of the sorption space is 413 Å.⁸

The older views on capillarity and a wide range of direct molecular attraction are summarized, for example, by Edser⁹ and Kremann.¹⁰

¹ G. Quincke, *Pogg. Ann. der Physik*, 1866, **127**, 16.

² G. Quincke, *Pogg. Ann. der Physik*, 1869, **137**, 402.

³ A. Schleiermacher, *Wied. Ann. der Physik*, 1879, **8**, 67; review of relevant literature to date.

⁴ J. Meyer, *Z. physik. Chem.*, 1920, **96**, 275.

⁵ A. M. Williams, *J. Oil Colour Chem. Assoc.*, 1922, **5**, 116.

⁶ L. I. Weber and G. Lewin, *Kolloid-Z.*, 1930, **50**, 197.

⁷ F. S. Goucher and H. Ward, *Phil. Mag.*, (6), 1922, **44**, 1002.

⁸ D. Reichinstein, *Z. anorg. allgem. Chem.*, 1927, **168**, 189.

⁹ E. Edser, *British Association Report on Colloid Chemistry*, 1922, **4**, 40.

¹⁰ R. Kremann, "Mechanische Eigenschaften flüssiger Stoffe," *Handbuch der allgem. Chemie*, 1928, **5**.

Hardy's remarkable studies on lubrication and adhesion have recently been summarized by himself.¹

(c) *Thick gaseous films*

Proof of the existence of thick gaseous films upon solid or liquid surfaces would afford a crucial demonstration of a wide range of direct molecular attraction since they could not be accounted for by any such mechanism as a chain of polarized molecules or multimolecular layers each binding its successor. Most, if not all, of the attempts in this direction have proved subject to re-interpretation as, for example, determinations of the effective radii of droplets or particles of colloidal dimensions when the possibility or probability of aggregation had been overlooked.

A *prima facie* case for the existence of thick films of air upon solid surfaces has been made out by Sir William Hardy.² The writer would refer to this experiment as "Mohamet's Coffin". A steel cylinder placed upon a steel plate is found to float upon a film of air of microscopic thickness of the order of 4,000 Å. deep. This film acts as a cushion between the two optically polished surfaces and is readily compressed but is spontaneously restored if the surfaces are sufficiently clean. The surfaces may be held in contact by contaminating them with a trace of liquid or grease and "wringing" them together; that is, forcing them together with a twisting or a sliding motion. The measurements consisted in a demonstration that the apparent height of the cylinder as measured from the plate to the top of the cylinder is about 4,000 Å. less when the cylinder has been wrung to the plate as compared with its position when the surfaces are clean and dry, no matter how much they may have been squeezed or forcibly

¹ W. B. Hardy, *Phil. Trans. Roy. Soc. London*, A, 1931, **230**, 1. See also the studies of insulating power of thin films by H. E. Watson and A. S. Menon (*Proc. Roy. Soc. (London)*, A, 1929, **123**, 185), L. Brüninghaus (*Compt. rend.*, 1929, **188**, 1386), and P. L. Copeland (*Phys. Rev.*, (2), 1930, **35**, 982).

² W. B. Hardy and M. Nottage, *Proc. Roy. Soc. (London)*, A, 1927, **118**, 209. See also C. Terzaghi, *Phys. Rev.*, (2), 1920, **16**, 54.

slid together. The writer has found in preliminary experiments with a much more refined differential method that this phenomenon actually occurs, but he is reluctant to admit the obvious inference of the existence of a microscopic range of direct molecular attraction without the opportunity for further tests for possible extraneous influences. Hardy had obtained a similar result with liquid films, but these, of course, are subject to the alternative explanation of polarization transmitted from molecule to molecule in the liquid, a mechanism which is inconceivable for gases.

Reference may be made to the experiments of Drucker¹ who found that the friction exhibited in the flow of a mixture of gases through glass capillaries does not change linearly with change in the composition of the mixture. This he ascribes to selective sorption of the components and the resulting variation of the composition of the gas outwards from the surface.

¹ C. Drucker, *Z. physik. Chem.*, 1918, **92**, 289; *Z. Elektrochem.*, 1929, **35**, 640.

CHAPTER XI

MOBILITY IN SORBED FILMS

MOBILITY OF THE OUTSIDE LAYER OF A CRYSTAL

Many films of insoluble substances on water are highly mobile, like soap bubbles, in which the material is constantly in movement.¹ It is largely due to the work of Volmer and his collaborators that we are aware that a similar state of affairs may obtain upon the surface of solids.

In a simple but striking experiment in which mercury at -10°C . was allowed to vaporize across an evacuated space to a glass surface kept at -63°C . Volmer and Estermann² found that tiny, filmy crystals of mercury rapidly grew out from the glass surface. The thickness of the crystals was not over one ten-thousandth of their greatest width. The rate at which the mercury atoms in the vapour strike a surface of given area is known from the kinetic theory of gases.³ Further, they had shown⁴ that nearly all mercury atoms striking a liquid or a solid surface of mercury are held by it.

Now the remarkable fact appears that the large flat surface of the mercury crystals does not grow nearly as fast as it is receiving mercury atoms, whereas the narrow sides are growing a thousand times faster than mercury atoms are reaching them directly from the vapour. The only conclusion is that mercury atoms which arrive on the large flat surface travel along that surface and feed the rapidly growing sides.

Hence, atoms or molecules striking a crystal of the same

¹ See for example, A. S. C. Lawrence, *Soap Films*. Bell & Sons, Ltd., London, 1929.

² M. Volmer and J. Estermann, *Z. Physik*, 1921, 7, 13.

³ Knudsen equation; see Chapter XVIII.

⁴ M. Volmer and J. Estermann, *Z. Physik*, 1921, 7, 1.

material may move about on the surface until they either evaporate again or are built into the space lattice.

It was shown by Volmer and Adhikari¹ that small crystal needles of benzophenone arising in a drop of liquid benzophenone grow out through the surface as much as 0.1 mm. outside the surface of the liquid as is clearly shown by microscopic observation. Here again the material for the growth of the crystals outside the surface must have moved along the surface as an invisible, adsorbed film of benzophenone.

The most striking experiment of Volmer and Adhikari was in a sense the converse of that just described. A succession of drops of mercury was allowed to brush against the side of a sharp needle-like crystal of benzophenone. The mercury carries away benzophenone upon its surface and, of course, the side of the crystal wastes away. However, the point of the crystal, which is some small distance away from the part touched by the mercury, likewise rapidly disappears. This is not due to evaporation, because the phenomenon ceases when the mercury droplets do not quite touch the benzophenone.² Hence, upon the finished crystal of benzophenone there rests a mobile adsorbed layer of benzophenone.

It is by no means necessary to assume that all crystals are covered with an adsorbed layer. Paneth and Thimann³

¹ M. Volmer and G. Adhikari, *Z. Physik*, 1925, **35**, 170. See also J. Estermann and O. Stern (*Z. physik. Chem.*, 1923, **106**, 399; J. Estermann, *Z. physik. Chem.*, 1923, **106**, 403) who found that minute crystals of silver were forming on glass when the molecular stream supplying silver atoms was insufficient to form a continuous layer 1 Å. deep, and that, similarly, mercury films so formed were discontinuous.

² M. Volmer and P. Mahnert (*Z. physik. Chem.*, 1925, **115**, 239) showed that the amount of benzophenone spreading upon a mercury surface in one second during contact with a crystal was 18,000 times greater than the amount which could have been carried through the air.

³ F. Paneth and W. Thimann, *Ber.*, 1924, **57B**, 1215. I. Langmuir (*J. Am. Chem. Soc.*, 1916, **38**, 2261) shows that the surface of a crystalline solid of appreciable vapour pressure must be more or less completely covered by an amorphous surface layer one molecule deep, and discusses the extent to which this will occur in various cases. However, this was before Volmer's essential contribution that adsorbed films may be freely mobile.

found that naturally occurring crystals of galena did not yield a surface equilibrium with a radioactive isotope of lead (compare Chapter X, page 334). Presumably the crystals had become too perfect and possibly could only react on the edges. However, such galena could be activated by heating to higher and higher temperatures until, after it had sintered, it was like fresh, artificial lead sulphide. These differences are not accompanied by any change in the space lattice. Galena of geological age is distinguished by its high polish; its surface dissolves at one-sixth the rate of ordinary lead sulphide and it does not sorb methylene blue at all.

Several other minerals, such as heavy spar (barium sulphate), celestine (strontium sulphate), anglesite (lead sulphate) and bismuth, resembled galena in lesser degree; but the mineral crocoite (lead chromate) and several others were quite as active as freshly precipitated chemicals.

MOBILITY UPON GLASS SURFACES

Direct proof of movement of adsorbed benzophenone upon a glass surface was obtained by Volmer and Adhikari.¹ They allowed a stream of mercury droplets to brush against the edge of a thin piece of glass upon which benzophenone had been crystallized but at a distance of 0.1 to 1 mm. from the edge which came in contact with the mercury. Nevertheless, the mercury carried away such appreciable quantities of benzophenone that it was necessary to conclude that the diffusion coefficient in the adsorbed layer is a hundred times greater than that in aqueous solution. It seems, however, to the writer that this conclusion must be confined to an interface between solid and gas; and that the ordinary slow diffusion must be observed in the interface between a solid and a liquid or between two liquids.

The rate of spreading upon a solid is one thousand ² times less than the corresponding rate upon a liquid; and the latter is therefore one hundred thousand times faster than diffusion through water. Oils, for example, take between

¹ M. Volmer and G. Adhikari, *Z. physik. Chem.*, 1926, **119**, 46.

² E. Landt and M. Volmer, *Z. physik. Chem.*, 1926, **122**, 404.

13 and 32 seconds to travel one metre upon the surface of clean water.¹ The initial velocity is greater, up to 25 cm. per second, as shown by Landt and Volmer's formula, $u = 42.8/\sqrt[3]{r}$, where u is the velocity in centimetres per second and r is the radius of the oil drop. It would be interesting to obtain the corresponding data for the rates of diffusion or persorption through permeable space lattices such as those referred to in Chapter V.

Volmer points out that an insoluble substance is carried along a liquid surface by a hydrodynamic streaming caused by the constant accession of new molecules of solvent to the surface; the friction on the air side is negligible. On the other hand, the atoms of a solid may only communicate thermal vibrations to adsorbed molecules and cannot leave their places.

Volmer's results have been confirmed by Moll² with phthalic anhydride, coumarin and diphenylmethane but not with paraffin and cetyl alcohol, using mercury droplets. It could be seen from the change in interference colours between crossed Nicols that a crystallized film of benzophenone or salol thins out even where it is not being touched by the mercury.

RELATION TO CHEMICAL REACTION, CATALYSIS AND CRYSTALLIZATION

Several writers have realized that mobility of sorbed molecules necessarily affects the laws governing rate of reaction and catalysis³ as well as some of the quantitative aspects of sorption. For example, Wilkins⁴ found evidence for lateral movement of oxygen upon a copper surface during its oxidation. Similarly, Bodenstein⁵ has pointed out that it involves a re-interpretation of his well-known studies of the formation

¹ See, for example, P. Woog, *Compt. rend.*, 1922, **174**, 162. A. Cary and E. K. Rideal, *Proc. Roy. Soc. (London)*, A, 1925, **109**, 301; E. Landt and M. Volmer, *Z. physik. Chem.*, 1926, **122**, 398.

² F. Moll, *Z. physik. Chem.*, 1928, **136**, 183.

³ H. Cassel, *Naturwissenschaften*, 1926, **14**, 103.

⁴ F. J. Wilkins, *Proc. Roy. Soc. (London)*, A, 1930, **128**, 407.

⁵ M. Bodenstein, *Z. physik. Chem.*, Abt. B, 1929, **2**, 345.

of sulphur trioxide by the contact process.¹ Again, on the same basis, the writer would explain Essin's² observation that during the electrolytic formation of persulphate the distance between sulphate ions capable of polymerizing on the anode surface is as much as 100 Å., without the necessity of assuming any such range of direct molecular attraction.

In general then, the sorbed layer may contain molecules derived both from the gas and from the solid itself. Cassel³ points out that during sorption of a gas, molecules of adsorbent may be displaced from the sorbed layer to take up positions in new planes of the crystal lattice on the surface of which more gas may be adsorbed or, on the other hand, more molecules of the solid may be attracted into the sorption layer. Hence a crystal surface will not, in general, be perfect, but will be rough, on a molecular scale. Cassel has also applied the new conceptions to the effect of admixtures upon the rate of crystallization of undercooled liquids.⁴ Smekal⁵ has developed from it the conception of "interstitial" electrical conductivity in solid electrolytes consisting of a conglomerate of crystal grains; and Murphy and Lowry discuss it more generally for all bodies of micellar or crystallite structure from the standpoint of the classical theory.

Mobility in sorbed films is an inevitable consequence of the classical theory of sorption (see Chapter XVII), although it would appear to have escaped attention for over a century. In Volmer's hands it becomes an important addition to the Langmuir theory of monomolecular sorption (Chapter XVIII). Langmuir himself had by 1925 arrived at the conclusion⁶

¹ M. Bodenstein and C. G. Fink, *Z. physik. Chem.*, 1907, **60**, 1.

² O. Essin, *Z. Elektrochem.*, 1928, **34**, 758.

³ H. Cassel, *Z. Elektrochem.*, 1928, **34**, 536.

⁴ H. Cassel, *Ergebnisse der exakten Naturwissenschaften*, 1927, **6**, 122.

⁵ A. Smekal, *Physik. Z.*, 1925, **26**, 707; *Anz. Akad. Wiss. Wien*, 1926, **63**, 195; *Z. tech. Physik*, 1927, **8**, 203, 561; *Ann. der Physik*, (4), 1927, **83**, 1202; *Z. Physik*, 1927, **45**, 869. For further references see the recent thorough discussion by E. J. Murphy and H. H. Lowry, *J. Phys. Chem.*, 1930, **34**, 598.

⁶ I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc. (London)*, A, 1925, **107**, 72.

that monomolecular layers of sorbed caesium atoms upon a tungsten surface, even when held by chemical bonds, were exactly similar to films of insoluble substances upon water. Thus for sufficiently dilute sorbed films he deduced the ideal two-dimensional gas law: F (in dynes per centimetre) $= nkT$, corresponding to the three-dimensional ideal gas law $p = nkT$.

CHAPTER XII

SORPTION BY CELLULOSE ¹ DERIVATIVES AND OTHER NON-RIGID GELS AND JELLIES

SWELLING

The subject of the swelling of non-rigid gels and jellies has been submitted to comprehensive review by Katz ² and to this the reader is referred for a clear and fascinating account. The evidence given in Chapter XIII shows that swelling is a universal effect for all porous bodies including such materials as glass and metals. It is all a question of degree, from the almost inappreciable but significant results with indifferent rigid materials, through the limited swelling illustrated by wood in water, through the enormous distension of the swelling jellies, to the extreme case where complete solution of the solid is effected through resolution into its constituent micelles or molecules.

In the latter cases, the phenomena go beyond sorption because much of the liquid is merely mechanically enmeshed within the structure of micellar aggregates released from elastic strain much in the same way that a portion of air enters the rubber tube of a tyre when the completely deflated tyre is opened.

Some of the most important materials of industry and

¹ For a review of the literature on the sorption of smokes and fogs by cotton and woollen filters, see A. Åström, *Svensk Kem. Tid.*, 1929, **41**, 190. For 500 selected references to the chemistry and technology of cellulose, see R. E. Montonna, *Paper Trade J.*, 1928, **86**, No. 18, p. 61; *Tech. Assocn. Papers*, 1928, **11**, 84. See also H. LeB. Gray and C. J. Staud, *Chem. Reviews*, 1927, **4**, 355, who include 104 references.

² J. R. Katz, *Ergebnisse der exakten Naturwissenschaften*, 1924, **3**, 317-404; 1925, **4**, 154-213.

common life such as the textiles are embraced within the heading of this chapter. It is evidently impossible to do more than indicate the general characteristics of the sorption of vapours and gases by these substances, with the briefest reference to their interpretation. One is reminded of the exacting requirements of industry as compared with the less specialized interest of a purely scientific survey when one recalls that cotton, for example,¹ is bought and sold on an enormous scale upon the basis of a standard moisture content, which would not be satisfied by the study of the form of an isotherm or of its position relative to the theories of various investigators.

STRUCTURE

Within the last few years our conceptions of the structure of matter which none of the older crystallographers would ever have considered crystalline, have rapidly developed. It is now so evident that all non-gaseous matter owes so much of its properties to structure that an enlargement of our ideas and much greater discrimination in classification is required. Some writers now write of ordinary liquids in terms of crystalline structure. Room has to be found ² for the varying degrees of structure of true liquids as revealed by such properties as viscosity or by X-ray examination, for the more highly developed structures of their surfaces and of films thereon, for the structures of colloidal particles, for the several distinct kinds of liquid crystals such as the two mutually immiscible conic anisotropic liquid phases of soap solutions, for the structure of jellies and of glasses and for the much more regular structure of rubber, cellulose and wool. There is a tendency among present day X-ray investigators to call the latter crystalline whenever any definite spacings in the structure become evident.

The structure of cellulose and its derivatives appears now

¹ R. H. Pickard, *J. Am. Chem. Soc.*, 1931, **53**, 1610; see also *J. Textile Inst.* and *Memoirs of the Shirley Institute*.

² For a brief illustrated review of this subject, see J. W. McBain, *J. Chem. Educ.*, 1929, **6**, 2115.

to be fairly definitely established.¹ A fibre is a tube whose walls are made up of concentric shells of rhombic or slightly monoclinic crystallites.² The unit cell of a crystallite consists of four glucose residues. The glucose residues are amylene oxide rings strung together end to end in extremely long chains by primary valencies operating through oxygen bridges. Each chain is entirely constructed of primary valencies not accessible for sorption. The chains are held to parallel chains by residual affinity, van der Waals' forces, or polarization, and here is an opportunity for sorption. To show the arrangement, the spacings, and the unoccupied volumes, Meyer and Mark's diagrams drawn to scale are reproduced in figs. 110³ and 111.⁴

In ramie the chains are parallel to the length of the fibre, whereas the arrangement in cotton is less regular. The

¹ For references see K. H. Meyer and H. Mark, *Ber.*, 1928, **61B**, 593; O. L. Sponsler and W. H. Dore, *J. Am. Chem. Soc.*, 1928, **50**, 1940; 1931, **53**, 1639; *Colloid Sym. Mon.* (M. I. T., 1926), 1926, **4**, 174; O. L. Sponsler, *Naturwissenschaften*, 1928, **16**, 263; K. Freudenberg, *Liebig's Ann. der Chem.*, 1928, **461**, 130; F. D. Miles and J. Craik, *J. Phys. Chem.*, 1930, **34**, 2607; K. R. Andress, *Z. physik. Chem.*, Abt. B, 1929, **4**, 190; J. Eggert and F. Luft, *Z. physik. Chem.*, Abt. B, 1930, **7**, 468; J. J. Trillat, *Rev. gén. colloïdes*, 1928, **6**, 57, 89; *Compt. rend.*, 1928, **186**, 859; K. Hess and C. Trogus, *Naturwissenschaften*, 1930, **18**, 437; E. A. Hauser, *Ind. Eng. Chem.*, 1929, **21**, 124; K. Eckling and O. Kratky, *Naturwissenschaften*, 1930, **18**, 461; J. Scheiber, *Farbe und Lack*, 1928, pp. 334 and 346. Iodine partly penetrates cellulose fibres and partly extends their space lattice, like calcium carbonate and barium sulphate (J. Strachan, *Nature*, 1930, **125**, 671). Sodium chloride and sodium tungstate sorbed on starch and filter paper exhibit no X-ray pattern (R. H. Aborn and R. L. Davidson, *Nature*, 1928, **122**, 440). See also K. Hess, C. Trogus, N. Ljubitsch and L. Akim, *Kolloid-Z.*, 1930, **51**, 89. W. H. Eccles and W. Bragg, *Proc. Roy. Inst. Gt. Britain*, Advance copy, January 24, 1930, 16 pp.; O. L. Sponsler, *Nature*, 1930, **125**, 633; W. H. Bragg, *Nature*, 1930, **125**, 634; M. Steude, *Nitrocellulose*, 1930, **1**, 32.

² For discussion of the fatty or waxy impurities see P. P. von Weimarn and collaborators (*Repts. Imp. Ind. Research Inst.*, Osaka, Japan, 1927, **8**, No. 6, p. 19).

³ K. H. Meyer and H. Mark, *Ber.*, 1928, **61B**, 600, figs. 1A, 1B, 2A, 2B.

⁴ K. H. Meyer and H. Mark, *Ber.*, 1928, **61B**, 601, fig. 6.

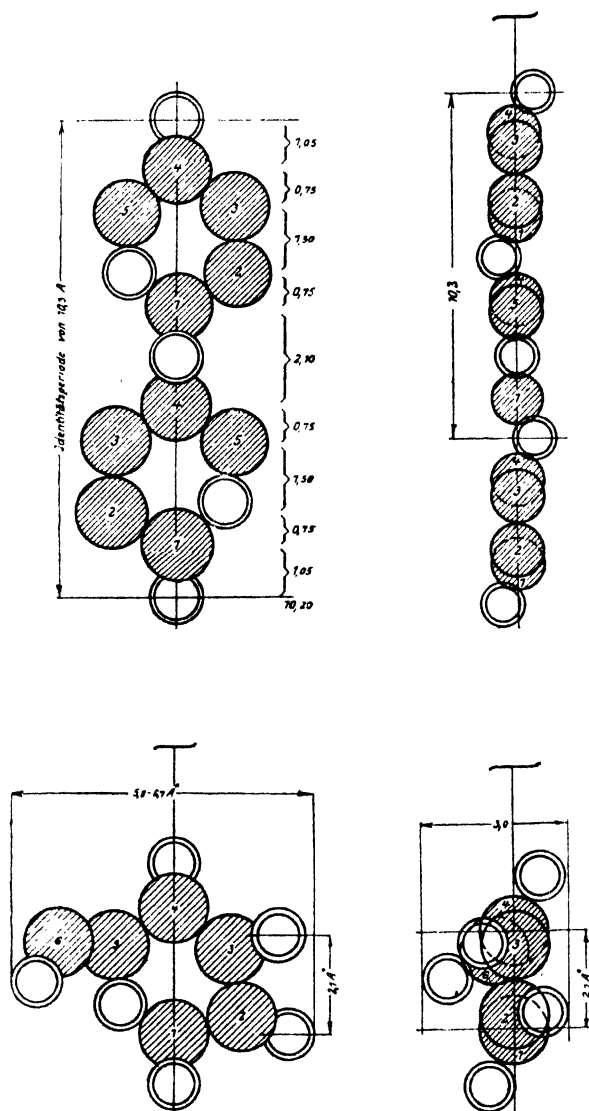


Fig. 110.—Dimensions and Spacings of a Chain of Glucose Residues in Mercerized Ramie Cellulose.

cellulose derivatives, hydrocellulose and oxycellulose, resemble cellulose but the hydrate, nitrate ¹ or acetate, of course, shows

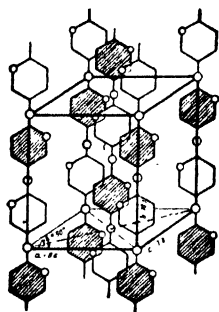


Fig. 111.—Spatial Arrangement of Cellobiose Chains in Cellulose.

definite displacements and rearrangements of the chains, there being two fundamental arrangements represented by cellulose and mercerized cellulose, respectively. ² Solvents not only dismember the fibres into separate crystallites but may penetrate the crystallites, enlarging the unit cell, and may even split them into molecular threads. ³

SORPTION OF WATER BY CELLULOSE

Sheppard and Newsome ⁴ consider that the sorption of water by cellulose and its derivatives is largely conditioned by the hydroxyl groups of the cellulose structure. In hydrate cellulose they are less mutually satisfied than in cellulose and are therefore more available for attracting polar molecules. ⁵ Nitration, esterification or ether formation greatly diminishes the sorption of water. In the case of the nitrates examined by Will ⁶ he found that the sorption of moisture is related by an empirical equation to the percentage of nitrogen, N , by the formula

$$W = \frac{334.4 - 23.65N}{31.11 - N}$$

where W is the moisture regain in per cent. Complete acetylation, however, still leaves an appreciable sorption of water,

¹ See, for example, H. Brunswig, *Z. ges. Schiess-Sprengstoffw.*, 1928, **23**, 337, 384.

² See, for example, K. R. Andress, *Z. physik. Chem.*, Abt. B, 1929, **4**, 204.

³ S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, 1929, **33**, 1826; S. E. Sheppard, *J. Phys. Chem.*, 1930, **34**, 1041.

⁴ S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, 1929, **33**, 1826; 1930, **34**, 1158.

⁵ For discussion of the effects of tension on mercerization and reactivity, see A. J. Hall, *Am. Dyestuff Repr.*, 1930, **19**, 417.

⁶ W. Will, *Mitt. Schiess. v. Sprengstoff. Neubabelsberg*, 1904.

whereas complete acetylation of glucose to penta-acetate or of cellobiose to octa-acetate reduces the sorption of moisture to the very small amount of 1 to 2 per cent at saturated humidity.

Cellulose nitrate can easily be prepared from solution in white opaque porous form which may show double the sorption of the transparent form.

Typical values for the sorption of moisture were obtained by Sheppard and Newsome with the McBain-Bakr sorption balance shown in fig. 112.¹ Some of their values are given in fig. 113.² It will be noted that oxycellulose and hydro-cellulose sorb distinctly less water than standard cellulose or cotton linters, whereas hydrate celluloses sorb about half as much again as the latter (in the limit 23 per cent compared with 16 to 18 per cent).³ The water is

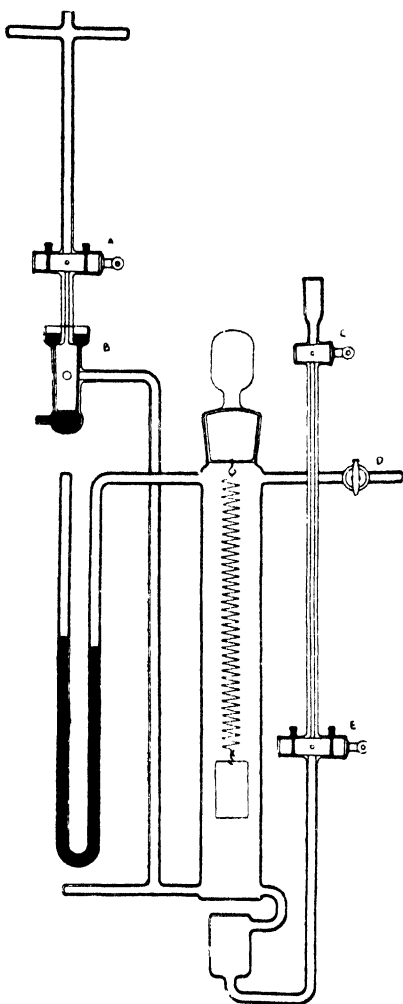


Fig. 112.—Sheppard and Newsome's Arrangement of the McBain-Bakr Balance for the Measurement of the Sorption of Solvents.

¹ S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, 1929, **33**, 1818, fig. 1.

² S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, 1929, **33**, 1820, fig. 2.

³ Compare also C. G. Schwalbe, *Z. angew. Chem.*, 1909, **22**, 197; *Die Chemie der Cellulose* (Borntraeger, Berlin, 1911).

attached to the free hydroxyl groups but a further portion is not so held and may be capillary water or built up layers or chains. "Since cellulose colloids do not form completely rigid, but elastic gels, which deform and swell on adsorption, it is probable that the ratio of free hydroxyls to bound

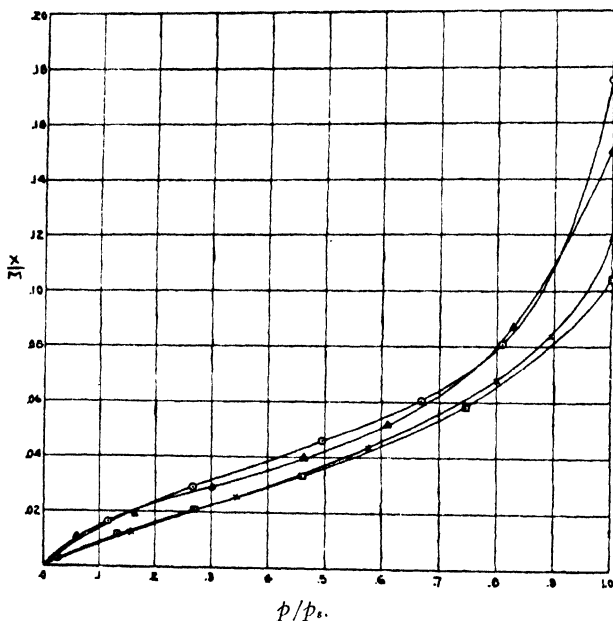


Fig. 113.—Sorption of Water at 30°C. by Cellulose. ○—standard cellulose; x—oxycellulose; △—cotton linters; □—hydrocellulose.

hydroxyls increases with adsorption of water, and decreases again on desorption, with a concomitant change of the 'pore space'."¹

¹ S. E. Sheppard and P. T. Newsome, *J. Phys. Chem.*, 1930, **34**, 1165 (rate of sorption). For similar views, see F. T. Peirce, *J. Textile Inst.*, 1929, **20**, T133; also S. Oguri and M. Nara, *J. Soc. Chem. Ind. Japan*, 1930, **33**, 267. In Sheppard and Newsome's experiments sorption was practically complete in about two hours, whereas in the presence of air the heat of sorption, which is of the same magnitude as the heat of condensation, is evolved for hours. O. Masson (*Proc. Roy. Soc. (London)*, 1904, **74**, 230) and O. Masson and E. S. Richards

Members of the Shirley Institute had arrived at similar views. The following is an abstract of Urquhart's ¹ paper on this subject. Since cotton is an elastic rather than an unelastic gel, the hysteresis in its adsorption isotherm for water cannot be accounted for by Zsigmondy's theory of curvature of the liquid meniscus in capillary spaces. The theory is advanced that adsorption of water takes place at the hydroxyl groups of the long, spiral, somewhat flexible molecules of cellulose and that on drying there is a tendency for twisting and rearrangement of the molecules or micelles so that the residual valencies of the hydroxyl groups mutually satisfy each other, thereby reducing the hygroscopicity. During re-absorption there is a tendency to return to the original orientation, the reproducibility of the hysteresis loop being thereby explained. In the formation of the cotton hair the cellulose is precipitated in the presence of water, and the cotton as it is taken from the boll is in consequence exceptionally active; the first drying produces a permanent reduction in hygroscopicity. Thereafter drying and reabsorption curves are reproducible. Heating cotton in a dry atmosphere reduces the hygroscopicity by favouring the mutual satisfaction of the residual valencies of the hydroxyl groups; heating in the presence of water increases the hygroscopicity by releasing the hydroxyl groups from each other's influence.

Definitive measurements ² of the sorption and desorption of the water vapour by cellulose as well as soda-boiled and mercerized cellulose have been made by Urquhart and Williams.³ Some of their results are reproduced in figs. 114,⁴

(*Proc. Roy. Soc. (London), A*, 1906, **78**, 412), using cotton, observed the same hysteresis as discovered by J. M. van Bemmelen (*Z. anorg. Chem.*, 1897, **13**, 234; *Die Absorption*, p. 233). J. H. Lester (*J. Soc. Chem. Ind.*, 1902, **21**, 388) showed aqueous extract of raw cotton more hygroscopic than cotton itself.

¹ A. R. Urquhart, *J. Textile Inst.*, 1929, **20**, T125.

² See R. H. Pickard, *J. Am. Chem. Soc.*, 1931, **53**, 1610.

³ A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, 1924, **15**, T138, T433; 1925, **16**, T155.

⁴ A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, 1924, **15**, T146, fig. 3.

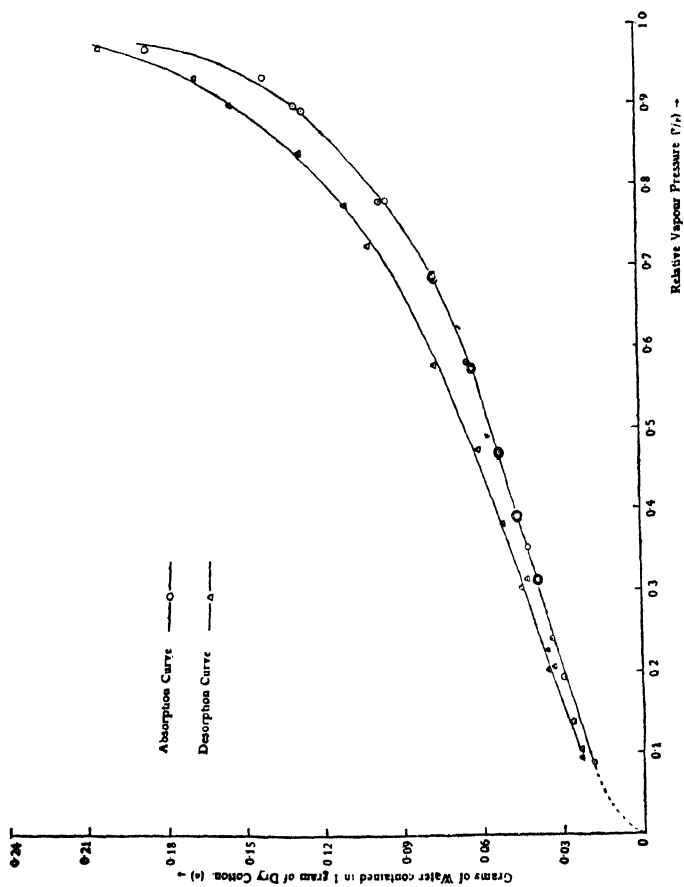


Fig. 114.—Sorption and Desorption of Water at 20° C. by soda-boiled Cotton 85R dried at 15° C.

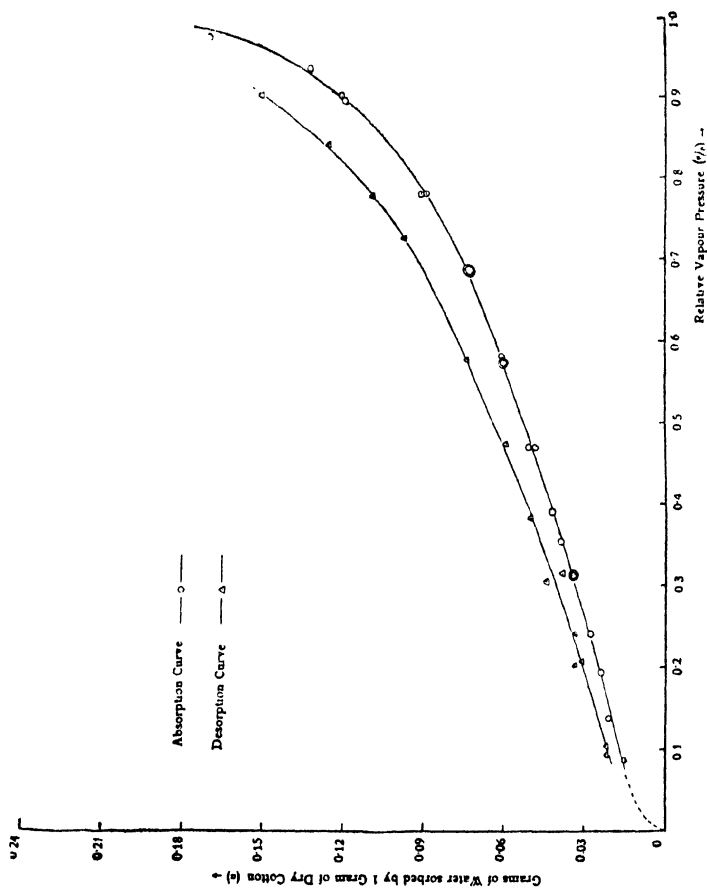


Fig. 115.—Sorption and Desorption of Water at 20°C. by soda-boiled Cotton 85R dried at 110°C.

115,¹ 116,² and 117.³ The very neat sorption pipette designed for this purpose is illustrated in fig. 118.⁴ It will be seen from their papers that there is a definite hysteresis between sorption and desorption and that heating or boiling with

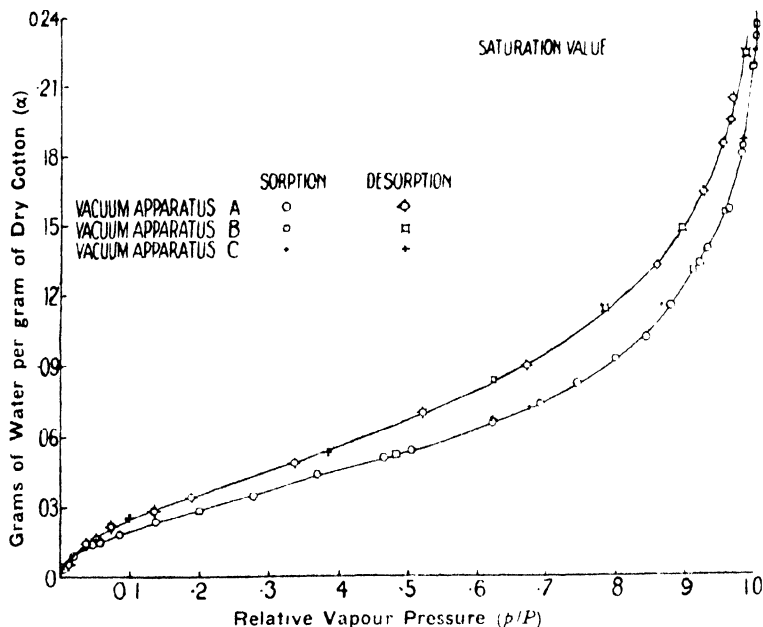


Fig. 116.—Sorption and Desorption of Water by soda-boiled Cotton 85R at 25°C.

soda reduces the amount of water sorbed. Cotton mercerized without tension in 15 per cent sodium hydroxide or 28 per cent potassium hydroxide has a maximum hygroscopicity,

¹ A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, 1924, **15**, T146, fig. 4.

² A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, 1924, **15**, T438, fig. 3.

³ A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, 1925, **16**, T158, fig. 1.

⁴ A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, 1924, **15**, T434, fig. 1.

being between 1.45 and 1.57 times that of the original unmercerized cotton.

Comparison of the amounts of various substances taken up

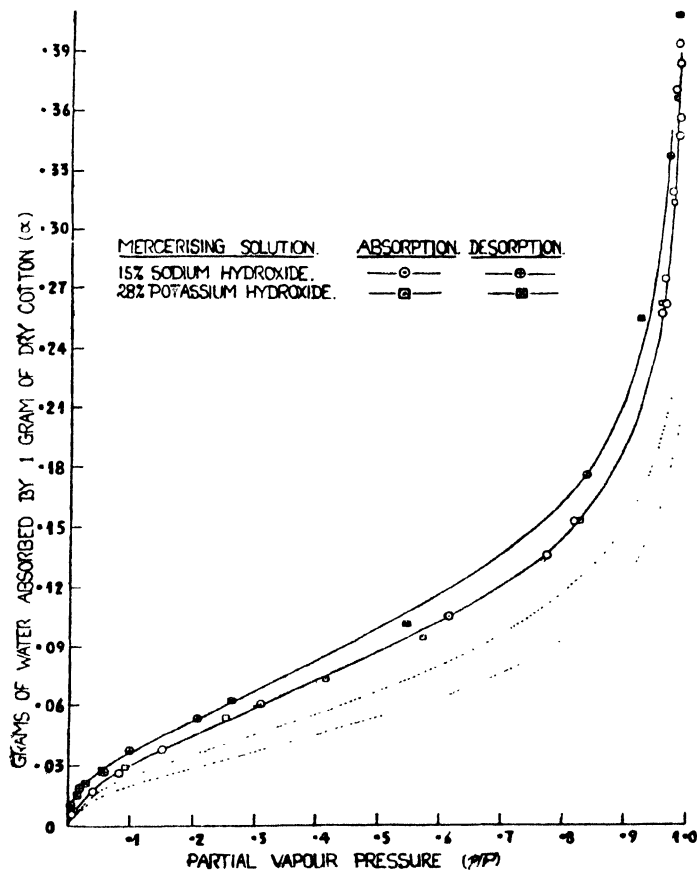


Fig. 117.—Sorption and Desorption of Water by Mercerised Cottons, at 25° C.

from saturated vapour by cotton has been made by Brimley¹ with the following results (table 46) given in per cent by weight of the cotton.

¹ R. C. Brimley, *Nature*, 1924, **114**, 432. See also this chapter, page 377.

TABLE 46
Sorption of various Vapours by Cotton

Saturated vapour	Unbleached cotton	Bleached cotton
	Per cent	Per cent
Water	18 to 20	19 to 21
Glacial acetic acid	18 to 20	17 to 19
Absolute alcohol	3 to 3½	8½ to 9
Carbon disulphide	1½ to 2	1½ to 2
Benzene	1½ to 2	1 to 2
Ether	7 to 7½	7 to 7½
Nitrobenzene	1½ to 2	1½ to 2
Acetone	2 to 2½	6½ to 7

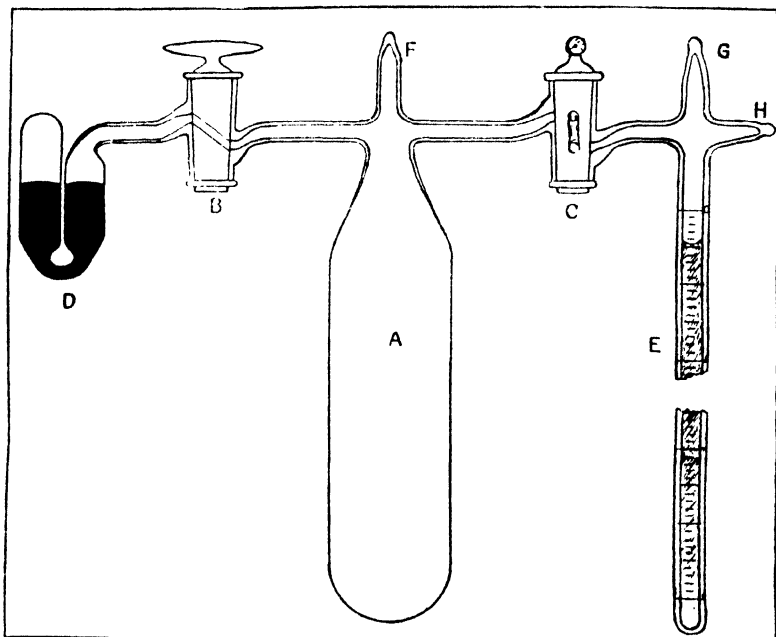


Fig. 118.—Sorption Pipette of Urquhart and Williams.

The sorption of water vapour by wood has been measured by Stamm,¹ who also found that 1 gm. of spruce wood sorbs 0.013 c.c. of hydrogen at 25° C. and 760 mm., 0.020 c.c. of nitrogen or 0.042 c.c. of oxygen.²

¹ A. J. Stamm, *Ind. Eng. Chem.*, 1927, **19**, 1021; *Ind. Eng. Chem.*, Analytical Ed., 1929, **1**, 94; 1930, **2**, 240; also L. M. Pidgeon and O. Maass, *J. Am. Chem. Soc.*, 1930, **52**, 1053; *Can. J. Research*, 1930, **2**, 318; but see R. H. Pickard, *J. Am. Chem. Soc.*, 1931, **53**, 1610.

² A. J. Stamm, *J. Phys. Chem.*, 1929, **33**, 405.

The writer is indebted to the Director of Research of the British Cotton Industry Research Association for forty-one further references to the moisture relations of cellulosic materials ¹ and to the Director of the Linen Industry Research Association for six references to flax.²

SORPTION BY NITROCOTTON

There is X-ray evidence ³ that the cellulose structure is partially or wholly retained through the nitration process so that sorption by these fibres might be expected to be similar to that of cellulose itself, which would explain the fact that the

¹ A. Abrams and W. A. Chilson, *Paper Mill*, 1930, **53**, No. 38, 24. K. Biltz, *Textil. Forschung*, 1921, **3**, 89. J. Boija, *Svensk. Pappers Tidshv.*, 1921, **24**, 298. E. Burlet, *Revue Text.*, 1928, **26**, 1699; 1929, **27**, 11; 1930, **28**, 877. H. F. Coward and L. Spencer, *J. Text. Inst.*, 1923, **14**, T28. H. F. Coward, L. Spencer and F. C. Wood, *J. Text. Inst.*, 1923, **14**, T529. G. F. Davidson and S. A. Shorter, *J. Text. Inst.*, 1930, **21**, T165. T. Fuwa, *Text. World*, 1923, **64**, 3577. E. Griffiths, *Proc. Phys. Soc.*, 1922, **34**, xlii. W. D. Harts-horne, *Trans. Nat. Assoc. Cotton Mfrs.*, 1911, **90**, 281; 1915, **98**, 254. J. J. Hedges, *J. Text. Inst.*, 1927, **18**, T350. R. O. Herzog, *Rayon Record*, 1930, **4**, 313. J. H. Lester, *Text. Merc.*, 1904, **31**, 440, 449. O. Masson and E. S. Richards, *Proc. Roy. Soc. (London)*, A, 1906, **78**, 412. H. R. Mauersberger, *Melliand*, 1930, **2**, 223. S. M. Neale, *J. Text. Inst.*, 1930, **21**, T225. O. A. Nelson and G. A. Hulett, *J. Ind. Eng. Chem.*, 1920, **12**, 40. J. Obermiller, *Z. angew. Chem.*, 1925, **38**, 838; *Melliand Textilber.*, 1925, **6**, 818. A. Rosenzweig, *Melliand Textilber.*, 1929, **10**, 365 (also flax). W. G. Schaposchnikoff, *Melliand Textilber.*, 1928, **9**, 844; 1930, **11**, 113, 197 (also flax). A. Scheurer, *Bull. Soc. Ind. Mülhouse*, 1900, **70**, 89; 1921, **87**, 129. T. Schloesing, Jr., *Bull. Soc. encour. ind. nat.*, 1893, 718. C. G. Schwalbe and E. Becker, *Zellst. u. Pap.*, 1921, **1**, 168. F. P. Slater, *J. Text. Inst.*, 1925, **16**, P53. Y. Toriyama, *J. Inst. Elec. Eng. Japan*, 1923, No. 420, 677. A. J. Turner, *J. Text. Inst.*, 1928, **19**, T101. A. R. Urquhart, *J. Text. Inst.*, 1923, **14**, T183; 1927, **18**, T55; 1929, **20**, T117. A. R. Urquhart and N. Eckersall, *J. Text. Inst.*, 1930, **21**, T499. A. R. Urquhart and A. M. Williams, *J. Text. Inst.*, 1926, **17**, T38. R. R. Williams and E. J. Murphy, *Bell Telephone Lab. Reprint*, B. 389, 1929.

² Those not cited elsewhere are A. Herzog, *Mitt. Forschungs-Inst.*, Sorau, 1920, **2**, 4; J. G. Crawford, *Reports Conditioning Sub-Committee 5th Congress Internat. Fed. Flax and Tow Spinners' Assoc.*, Ghent and Vienna, 1913 and 1914; M. H. Preston and J. A. Matthew, *Linen Industry Research Inst. Memoir*, 1929, **4**, No. 61, 195-235.

³ H. Brunswig, *Z. ges. Schiess-Sprengstoffw.*, 1928, **23**, 337, 384; F. D. Miles and J. Craik, *Nature*, 1929, **123**, 82; F. D. Miles and M. Milbourn, *J. Phys. Chem.*, 1930, **34**, 2598.

amount of sorption for any nitrocotton is more or less constant, reproducible and reversible as shown by different workers using different methods. Thus the values of x/m obtained with the McBain-Bakr ¹ balance are duplicated by the new sorption pipette of Jenkins and Bennett.² For example, at a 30°/20° C. temperature range a nitrocotton containing 12.3 per cent nitrogen sorbed 38.54 ³ per cent and 38.72 ⁴ per cent of its own weight of acetone vapour by the former method and 38.47 ² per cent by the latter.

The experiments carried out in the writer's laboratory have not yet been published,⁵ but the main conclusions of this work will be given briefly here.

(1) Equilibrium is easily attainable through direct and reverse experiment from both sides of equilibrium, hysteresis being negligible. For high relative pressures it is rapid, being only a few hours for a few solvents; several days may be required but in general it is complete in 24 hours, although the actual time depends upon the boiling points of the solvents used.⁶ Some experiments have been carried out over periods of a few months but, though the curves are all smooth, there is no final saturation value, the fibres continuing to take up traces of vapour over long periods.

(2) Sorption increases as the difference between the temperature of adsorbent and the liquid decreases. The 60° C. isotherms are all about two-thirds as great as the 30° C. values. For a constant difference of temperature the amount of sorption remains nearly constant.

(3) The sorption values do not follow the Langmuir straight-line relationship except up to half saturation in the case of such good solvents for nitrocotton as acetone, methyl ethyl ketone and ethyl alcohol. After half saturation the relation-

¹ A. M. Bakr and J. W. McBain, *J. Am. Chem. Soc.*, 1924, **46**, 2718.

² W. J. Jenkins and H. B. Bennett, *J. Phys. Chem.*, 1930, **34**, 2318.

³ R. Buckingham (unpublished).

⁴ D. P. Davies (unpublished).

⁵ Work on nitrocellulose was carried out in the Bristol Laboratory by A. M. Bakr, S. J. Good, H. K. Harrison, D. P. Davies, C. W. Hutchinson, H. J. Willavoys and R. Buckingham from 1923-1927 (unpublished).

⁶ L. Rubenstein, *J. Phys. Chem.*, 1930, **34**, 2330.

ship is reversed and we obtain crossing lines similar to those found by Bray and Draper,¹ the break in the curves for both acetone and methyl ethyl ketone being 0.33 per cent at 30° C. and 22 per cent at 60°.² The explanation here is wholly different from the case of Bray and Draper.¹ Whereas in their rigid oxides the pores were appreciably constant, with the nitrocellulose the structure is being progressively opened up through uncoupling of residual valencies, the bonds being satisfied with solvent molecules which are therefore increasingly sorbed at higher relative humidities. It is possible that there is no capillary condensed liquid present in the majority of cases but only monomolecular sorption and built up multimolecular layers.

For non- or semi-solvents such as benzene the Langmuir relationship holds. This is understandable when one considers the effect of the two types of compounds upon the nitro cotton. Acetone is an excellent solvent for nitro cotton and in contact with it causes the fibrous structure to break down and to go into solution, the so-called gelatinizing effect. The sorption of such vapours by nitro cotton is the same in its original fibrous state or in its gelatinized state. (Some experiments would indicate an even greater x/m when the nitro cotton is gelatinized.) On the other hand, for those substances which cannot disintegrate the fibres and form a gel or solution, the fibres act as would an inert charcoal or other rigid porous body and sorption follows the ordinary sorption laws. Thus for benzene, x/m is very low but the Langmuir relationship holds as in the case of charcoal.

(4) A generalization can be made to the effect that those substances which are known to be good solvents for nitrocellulose are extensively sorbed, whereas those substances termed bad or non-solvents are sorbed in only slight amounts.

Comparison of the swelling obtained by immersion of dry films of the same nitro cotton in liquids shows the same effect. For example, the percentage increases in volume for methyl

¹ W. C. Bray and H. D. Draper, *Proc. Nat. Acad. Sci.*, 1926, **12**, 295.

² D. P. Davies (unpublished).

and ethyl alcohols, which are fair solvents, are 1939 per cent and 1377 per cent, respectively, as compared with 1.4 per cent and 1.2 per cent for the semi-solvents, benzene and toluene, respectively.¹

Table 47 shows the approximate magnitude of the sorption for various vapours studied in the writer's laboratory. The pair of temperatures given in each of the last four columns refers to the temperature of the nitrocotton (30° and 60° C.) and to the temperature of the liquid whose vapour surrounds the nitrocotton. The temperatures chosen for quotation refer to moderately low and very high relative humidities. The terms used to describe the solvent power are debatable but rest upon a number of considerations. Put bluntly, the first six substances and methyl alcohol dissolve this nitro-

TABLE 47

Sorption of Organic Vapours by Propulsive Soluble Nitrocotton (12.3 per cent Nitrogen)

Vapour	Solvent power	x/m in per cent 30°/15° C.*	x/m in per cent 30°/29° C.	x/m in per cent 60°/30° C.	x/m in per cent 60°/59° C.
Iso-propyl acetate	Good	32.7	129	—	—
Methyl ethyl ketone	. Very good	28	88	13	73
Acetone	. Very good	26.2	85 (89 gel)	7.5	51.2
Methyl acetate	Good	33.8	100	—	—
<i>n</i> -Butyl acetate	Good	16.1	130	9.8	91.3
Methyl phenyl urethane	. Good	—	25.3	6.6	32.2
Benzyl alcohol	Semi	7.8	17.3	3.12	13.2
Ethyl alcohol	. Fair	5	13.5	2.6	9.6
Methyl alcohol	. Fair	4.4	16.1	0.37	7.4
Toluene	. Semi	0.6	11.9	2.7	7.3
Chloroform	. Fair	8.0	14.0	3.5	8.7
Benzene	. Semi	6.5 †	9.9	3.2	5.1
<i>n</i> -Butyl alcohol	Poor	2.2	4.9	0.51	2.54
Decane	. Poor	2.1	2.65	0.46	0.95
Iso-butyl alcohol	Very poor	1.2	2.3	0.27	3.48
<i>n</i> -Amyl alcohol	Very poor	1.1	2.4	0.16	1.89
Carbon tetrachloride	. Very poor	0.92	2.65	—	—
<i>n</i> -Octyl alcohol	Very poor	0.30	0.98	0.36	1.23
Cyclohexanol	. Very poor	0.36	3.04	0.5	7.4
Hexane	. Very poor	0.14	0.39	0.22	0.34

* Mean of actual values taken between 13°–17°.

† Willavoys obtained 7.7, Davies 8.5 (unpublished).

¹ H. J. Willavoys (unpublished).

cotton, the others do not. Ethyl alcohol has only to be chilled or admixed with other non-solvents to become a solvent.¹

It is interesting to note that nitrocotton sorbs somewhat more than its own weight of the best solvents but only a few per cent by weight of indifferent liquids.

Roughly equal volumes of various liquids of similar solvent power are sorbed by the same weight of nitrocotton but, whereas with non-solvents this may amount to 0.13 c.c. per gram of nitrocotton, with good solvents it lies between 1.0 and 1.5 c.c. per gram of nitrocotton at 30°, for practically saturated vapours in each case.

Rubenstein,² continuing Jenkins' and Bennett's work, established the fact that the amount of sorption increases with nitrogen content up to about 12.2 per cent and then decreases. There would appear to be a critical change in the properties of nitrocellulose at this point. Methyl alcohol is an exception because its sorption decreases with the percentage of nitrogen in the cellulose.

A good deal of attention has been paid in our laboratory to following up our early observation that a sorption isotherm at 30° could not be duplicated by any sample of nitrocotton if that sample had been raised in temperature to 60° for measurement there and again lowered to 20°. The subsequent readings were all low. However, further work on this so-called degradation phenomenon has led us to the conclusion that, although nitrocotton does change with heat treatment, in some cases developing an increasing capacity for vapour, in others a decreased ability, in due time the nitrocotton returns to normal, the degradation being reversible.

A further effect observed at 60° by Willavoys was that nitrocotton (after heating for a month at 60° C.) at first took up far more than it retained after several hours. Thus after four hours, an original sorption of 11.4 per cent acetone fell to 2.8 per cent and after a further 40 hours to 2.2 per cent.

¹ Compare J. W. McBain, L. E. Smith and C. E. Harvey, *J. Phys. Chem.*, 1926, **30**, 312.

² L. Rubenstein, *J. Phys. Chem.*, 1930, **34**, 2330.

This might be explained by a rearrangement of the structure and exposed groupings.

To conclude, prolonged heating of the nitrocotton does not permanently affect its sorbing power, although it may change it temporarily.

Calculation of the heat of sorption of the nitrocotton is rendered uncertain by the occurrence of "degradation", but the data suffice to show that the initial heat of sorption is much greater than the latent heat of condensation to liquid, the values falling towards the latter as the relative humidity approaches saturation. With already degraded samples the heat of sorption approaches the latent heat of condensation.

STARCH ¹

The writer has not chanced upon many references to sorption of gases and vapours by starch. However, the striking similarity between the S-shaped vapour pressure curves of aqueous solutions of sulphuric acid, alkali hydroxides, lithium chloride, calcium chloride, magnesium chloride, and phosphoric acid and the vapour pressure curves of swelling jellies in general² was illustrated for the particular case of starch by Rakovsky.³ At 10 mm. pressure of water vapour and 19° C. potato starch contained 19.6 per cent, wheat starch 14 per cent, and St. Vincent arrowroot starch 15 per cent of water, the maximum being roughly 35 per cent for potato, 27 per cent for wheat and 30 per cent for arrowroot and distinctly less at higher temperatures. The hygroscopic qualities of films of boiled starch, which show pronounced hysteresis, have been studied by Farrow and Swan.⁴

¹ For X-ray examination see O. L. Sponsler, *Am. J. Botany*, 1922, **9**, 471; E. Ott, *Physik. Z.*, 1926, **27**, 174; St. v. Náray-Szabó, *Liebig's Ann. der Chem.*, 1928, **465**, 299. For a general review see R. P. Walton, *A Comprehensive Survey of Starch Chemistry* (Chemical Catalogue Co., New York, 1928).

² J. R. Katz, *Ergebnisse der exakten Naturwissenschaften*, 1924, **3**, 317-404; 1925, **4**, 154-213.

³ A. V. Rakovsky, *J. Russ. Phys.-Chem. Soc.*, 1911, **43**, 170, 186, 362, 1762; 1915, **47**, 18, 1326; *Kolloid-Z.*, 1911, **9**, 225.

⁴ F. D. Farrow and E. Swan, *J. Textile Inst.*, 1923, **14**, T465; E. Swan, *J. Textile Inst.*, 1926, **17**, T527.

Boehm¹ noted the amounts of air, oxygen, nitrogen and carbon dioxide that could be taken up or extracted from cork, wood, starch, boiled potatoes, beets, charcoal and coal. Starch and sawdust sorb five or six volumes of carbon dioxide, cork much less. The carbon dioxide is not fully removed by evacuation at 98° C. but may be boiled out. In dry pores of cells carbon dioxide, oxygen and water vapour are sorbed. Moist starch and cellulose do not sorb carbon dioxide more than corresponds to their solubility in the water present.

Cellulose and starch sorb gases² in the order of their solubility in water, which is also the order of their sorption by charcoal; namely, ammonia, hydrogen chloride, sulphur dioxide, carbon dioxide, oxygen, hydrogen. The amount taken up by cellulose is almost 1 mol of ammonia or hydrogen chloride for 24 carbon atoms.³ In per cent by weight, the amounts sorbed were hydrogen chloride 5.1 per cent, ammonia 3.96 per cent, sulphur dioxide 1.40 per cent, and carbon dioxide 0.045 per cent. Guncotton sorbed 12.7 per cent of sulphur dioxide. Starch sorbs nearly twice as much³ hydrogen chloride gas as cellulose.

WOOL

Wool and hair consist of cells having an elastic wall enclosing fibrils, probably attached to the wall and to each other. The cell walls and the fibrils have recently been shown by X-ray examination to possess a periodic structure.⁴ Astbury and Woods' diagram is reproduced in fig. 119.⁵

Speakman⁶ has shown that the lamellar micelles in wool

¹ J. Boehm, *Botan. Ztg.*, 1883, **41**, 521, 537, 553.

² B. Oddo, *Gazz. chim. ital.*, 1919, **49**, 127.

³ D. Costa, *Gazz. chim. ital.*, 1924, **54**, 207; *Ann. chim. applicata*, 1926, **16**, 636. See also G. L. Stadnikov, *J. Russ. Phys. Chem. Soc.*, 1916, **48**, 301.

⁴ For references see J. Ewles and J. B. Speakman, *Proc. Roy. Soc. (London)*, B, 1930, **105**, 600; J. B. Speakman, *J. Textile Inst.*, 1927, **18**, T431; W. T. Astbury and H. J. Woods, *Nature*, 1930, **126**, 913; J. R. Katz, *Proc. Acad. Sci. Amsterdam*, 1924, **27**, 505; W. T. Astbury and A. Street, *Trans. Roy. Soc. (London)*, A, 1931, **230**, 75.

⁵ W. T. Astbury and H. J. Woods, *Nature*, 1930, **126**, 913, fig. 1.

⁶ J. B. Speakman, *Nature*, 1930, **126**, 565; also *J. Soc. Chem. Ind.* 1930, **49**, 209T; *Trans. Farad. Soc.*, 1930, **26**, 61.

fibre are "relatively if not entirely impervious to molecules as small as the water molecule". Their thickness is of the order of 200 Å. with pores of the order of 40 Å. between them. When the fibre is swollen in water, the length of the fibre is increased 1.1 per cent and the diameter 18 per cent. Methyl alcohol or methylene glycol enter and swell the fibre, opening the pores until they can admit such molecules as octyl alcohol.

The sorption of water by wool exhibits the same S-shaped isotherms as were noted in the sorption of solvents by nitro-cotton. The technical term for x/m expressed in parts by weight of moisture per 100 gms. of material dried at 105° C. is "moisture regain". For standard conditions in Bradford, England,¹ this amounts to 14 per cent for noils, 16 per cent for cloth or scoured wool, 18½ per cent for yarns dry or oiled or for dry tops, and 19 per cent for tops in oil. The United States standard for natural wool regain is 13.75 per cent as compared with a standard of 17 per cent suggested by the International Conference. It will be noticed that the moisture regain of wool² at 67 per cent relative humidity is double that of cotton. It diminishes with rise of temperature and of course

¹ Compare S. G. Barker and J. J. Hedges, *J. Textile Inst.*, 1926, **17**, T453.

² T. Schloesing, Jr., *Compt. rend.*, 1893, **116**, 808; *Bull. soc. encour. l'ind. nat.*, 1893; *Textile World Record*, Boston, Nov., 1908 (also silk and cotton); W. D. Hartshorne, *Trans. Nat. Assoc. Cotton Manufacturers*, 1905, **79**, 194; *Amer. Dyestuff Repr.*, 1924, **13**, 37; A. M. Wright, *J. Soc. Chem. Ind.*, 1909, **28**, 1020; A. Scheurer, *Bull. Soc. ind. Mulhouse*, 1900, **70**, 82; 1921, **87**, 129; A. Woodmansey, *J. Soc. Dyers Colourists*, 1918, **34**, 227; R. Kimura, *Arch. f. Hyg.*, 1922, **91**, 183 (also retentivity for ammonia). S. A. Shorter and W. J. Hall, *J. Textile Inst.*, 1924, **15**, T305 (the hygroscopic capacity of wool in different forms and its dependence upon atmospheric humidity, etc.); F. T. Trouton and B. Pool (*Proc. Roy. Soc. (London)*, A, 1906, **77**, 292) used flannel; M. W. Travers (*Z. physik. Chem.*, 1907, **61**, 241; *Proc. Roy. Soc. (London)*, A, 1907, **79**, 204) used cotton and wool; V. Lohrmann, *Kiserlet Kozlemenyei*, 1927, **30**, 472; A. V. Rakovsky (*J. Russ. Phys.-Chem. Soc.*, 1915, **47**, 18) used cotton, wool, filter paper, flax and hemp. T. Kujirai, Y. Kobayashi and Y. Toriyama (*Rikwagaku Kenkyujo Iho*, 1923, **2**, 105; *Sci. Papers Inst. Phys. Chem. Res.*, 1923, **1**, 79) studied the sorption of moisture by nine insulating materials and found it accorded with the Langmuir formulation and, like Rakovsky, also found hysteresis as did T. Fuwa and A. P.

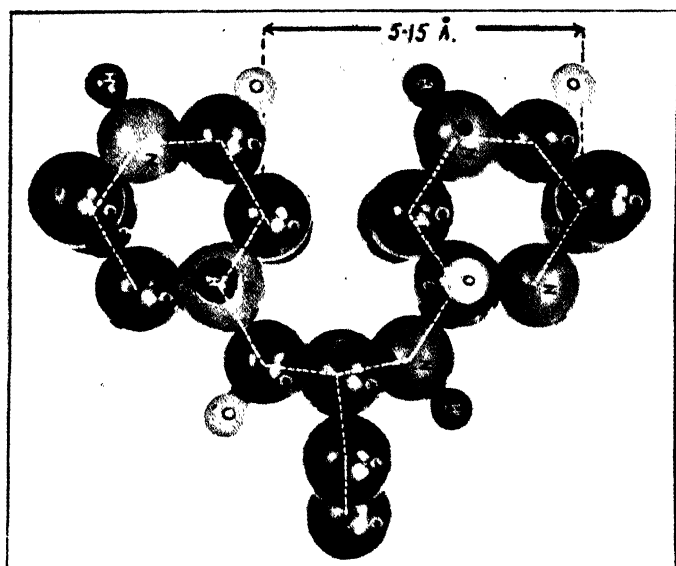


Fig. 119. Portion of space model of wool or human hair.

increases with relative humidity as may be seen in table 48. Scheurer gives the amount of water sorbed from a saturated atmosphere as 19–20.2 per cent for cotton, 28–29.8 per cent for silk and 33.3–35.3 per cent for wool; whereas Kimura found 19.8–20.0 per cent for cotton, 28.2–28.7 per cent for wool, 22–24 per cent for wood, 15.6–24.9 per cent for paper and 20.2–20.5 per cent for linen.

TABLE 48

Sorption of Water Vapour by Wool in grams per 100 gms. Dry Wool

Relative humidity	43.3	55.4	62.3	74.6	81.5	86.2	90.0
Shorter and Hall ¹	13.12	15.62	16.72	10.01	19.02	20.3	22.47
Schloesing ²	12.50	14.20	15.0	17.50	19.40	21.50	24.0
Hartshorne ³	11.60	14.00	15.50	18.50	20.40	22.10	23.60

Standard values for moisture regain of wool in its various forms are given by Shorter and Hall ¹ and quoted in a rearranged table by Barker.⁴

The two sorption isotherms expressed in moisture regain by Hedges are given in fig. 120.⁵ It is seen from the figure that the heat of sorption is greater than the latent heat of condensation and this was confirmed by direct measurement, the heat falling off with increase of sorption.

Speakman ⁶ has shown that the percentage by weight of water sorbed is the same for wool as for wool which has been progressively destroyed by sodium sulphide even when the wool residue had lost over half its weight. For untreated, purified wool he found that at 24.2 per cent, 73.5 per cent, and 91.3 per cent relative humidity, the per cent by weight of water sorbed was 6.80, 17.00, and 24.83, respectively. Wool stretched under water sorbs slightly more than unstretched wool.⁷

Godbout (*Textile World*, 1923, **64**, 3023). E. Müller (*Dinglers polytech. J.*, 1882, **245**, 210; *J. Soc. Chem. Ind.*, 1882, **1**, 356) found the ratio between moisture in air and in fabrics.

¹ S. A. Shorter and W. J. Hall, *J. Textile Inst.*, 1924, **15**, T312.

² T. Schloesing, Jr., *Compt. rend.*, 1893, **116**, 808; *Textile World Record*, Boston, Nov., 1908.

³ W. D. Hartshorne, *Trans. Nat. Assoc. Cotton Manufacturers*, 1905, **79**, 194; *Am. Dyestuff Repr.*, 1924, **13**, 37.

⁴ S. G. Barker, *Trans. Inst. Chem. Eng.*, 1928, **6**, 166.

⁵ J. J. Hedges, *Trans. Farad. Soc.*, 1926, **22**, 186, fig. 4.

⁶ J. B. Speakman, *Nature*, 1930, **126**, 565.

⁷ J. B. Speakman, *Nature*, 1929, **124**, 411.

The writer is indebted to the Director of Research of the Wool Industries Research Association and to Miss M. H. Norris, M.Sc., for forty-one further references bearing upon the sorption of moisture by wool¹ and for four references

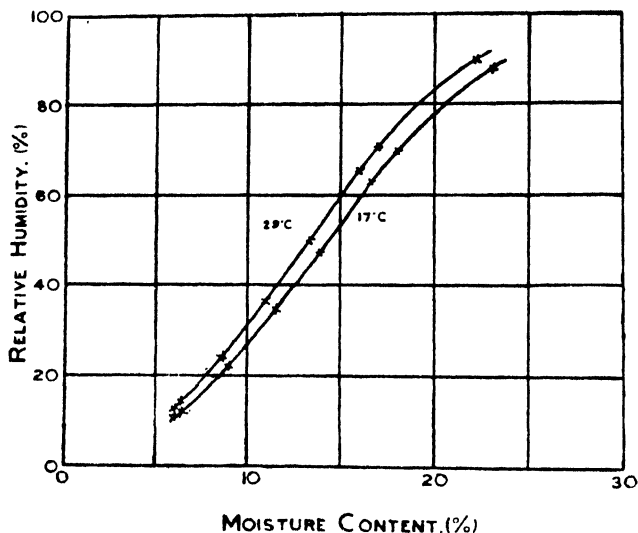


Fig. 120.—Sorption of Water Vapour by Wool in grams per 100 gms. of Dry Wool.

¹ S. G. Barker, *Trans. Inst. Chem. Eng.*, 1928, **6**, 162; *Wool: A study of the fibre*, 1929, pages 46–67 (H.M. Stationery Office, London). S. G. Barker and J. J. Hedges, *Dyer and Calico Printer*, 1927, **57**, 152. J. Barker and L. P. Priestley, *J. Text. Inst.*, 1925, **16**, P272. J. Barritt and A. T. King, *J. Text. Inst.*, 1926, **17**, T386. E. G. Bryant, *Chem. News*, 1913, **108**, 85 (ordinary tweed containing 12–14 per cent of water). E. Burlet, *Rev. Text.*, 1930, **28**, 877 (scoured wool, cotton thread and natural silk). W. H. Doherty, *Chem. News*, 1914, p. 254 (cloths at different temperatures and humidities). E. A. Fisher, *Proc. Roy. Soc. (London)*, A, 1923, **103**, 139 (evaporation from wool, sand and clay). H. Fleming, *Textile Colorist*, 1928, **50**, 253. E. A. Garrett, *Eng. Patent No.* 29512. W. D. Hartshorne, *Trans. National Assoc. Cotton Manufacturers*, 1911, No. 90, 281; *Bull. National Assoc. Wool Manufacturers*, 1915, **45**, 93; 1921, **51**, No. 4, 369; *Trans. Amer. Soc. Mech. Eng.*, 1917, **39**, 1073. J. A. Hill, *Wyoming Agric. Exptl. Sta. Bull.*, 1922, No. 132. A. T. King, *J. Text.*

each to the sorption of chlorine¹ and of sulphur dioxide,² which are sorbed to the extent of many per cent by weight.

SILK

Further to the work on hygroscopicity of silk due to Müller, Sheurer, Wilson and Fuwa, Schloesing fils, Kujirai, Kobayashi and Toriyama, to which reference was already given, the writer is indebted to the Director of Research of the British Silk Research Association for reference to that of Obermiller

Inst., 1926, **17**, T53; *Trans. Faraday Soc.*, 1929, **25**, 451. S. N. Kowalewsky, *Melliand*, 1930, **2**, No. 4, 539. H. R. Mauersberger, *Melliand*, 1930, **2**, No. 2, 223 (rayon, silk, wool, linen, cotton). J. Obermiller, *Z. angew. Chem.*, 1925, **38**, 838; J. Obermiller and M. Goertz, *Melliand Textilber.*, 1926, **7**, 71 (regain of textiles and humidity). R. G. Parker and D. N. Jackman, *Brit. Launderers' Res. Assoc.*, 1926. Publication No. 24 (regains and rates for cotton, linen, silk, artificial silk and wool; also water retained, up to 2 per cent, after drying over P₂O₅). E. A. Parnell, *The Life and Labours of John Mercer*, 1886, Longmans, Green & Co., London. H. Priestman, unpublished (regain of tops). A. Rosenzweig, *Melliand*, 1929, **1**, No. 6, 870; *Melliand Textilber.*, 1929, **10**, 4E, 225 (cotton, silk, wool, artificial silk, flax, hemp and jute). W. G. Schaposchnikoff, *Melliand Textilber.*, 1928, **9**, 844; *Melliand*, 1929, **1**, No. 3, 385; No. 4, 517 (extensive tables for cotton, wool, silk, artificial silk, flax, hemp and jute). S. A. Shorter, *J. Soc. Dyers and Colorists*, 1920, **36**, 299 (wool at various temperatures and humidities); 1923, **39**, 270 (wool); *J. Text. Inst.*, 1924, **15**, T328 (thermodynamics). S. A. Shorter and W. J. Hall, *W.I.R. Assoc. Publications*, 1924, No. 33; 1925, No. 47 (effects of chlorination and sulphur dioxide on regain of hosiery). S. A. Shorter, H. R. Hirst and W. J. Hall, *W.I.R.A. Publications*, 1924, No. 41 (effect of dyeing, etc.). H. Sommer, *Melliand Textilber.*, 1928, **9**, 214; 1929, **10**, 4E, 242 (regain of textiles). J. B. Speakman, *Proc. Roy. Soc. (London)*, B, 1928, **103**, 377; *Trans. Faraday Soc.*, 1929, **25**, 92. A. E. Stacey, *Textile World*, 1927, **72**, 2529 (textile regain compared with physical properties).

¹ E. Knecht, C. Rawson and R. Loewenthal, *Manual of Dyeing*, 1917, Vol. I, p. 56 (C. Griffin & Co., Ltd., London) (dry chlorine no action on dry wool). L. Meunier and H. Latreille, *J. Soc. Dyers and Colorists*, 1924, **40**, 266; *Chim. et Ind.*, 1923, **10**, 636 (dry chlorine sorbed by wool). S. R. Trotman and E. R. Trotman, *J. Soc. Chem. Ind.*, 1926, **45**, 111T; S. R. Trotman and C. R. Wyche, *J. Soc. Chem. Ind.*, 1924, **43**, 293T.

² J. L. Raynes, unpublished (rate at different humidities); summary in *W.I.R.A. Publications*, 1926, No. 60, 11. A. Reyckler, *Bull. Soc. Chim. Belg.*, 1909, **23**, 471; *J. Chim. Phys.*, 1910, **8**, 3.

and Goertz,¹ Hönig,² Sommer,³ and Stolze;⁴ together with the following data⁵ for other gases showing the volume of gas sorbed by one kilogram of silk:

Gas.	NH ₃	HCl	SO ₂	H ₂ S	CO ₂	CO	N ₂	H ₂
Litres	30	25	25	15	10	2	1	0.5

The findings of the British Silk Research Association as to moisture regain of silk at 25° C. are summarized as follows, based upon dry weights, found by long exposure over phosphorus pentoxide at 25°. The moisture regains of degummed "isoelectric" Chinese, Japanese, and Italian silks agree within 0.1 per cent, and are 9.2 and 10.0 per cent for absorption and desorption respectively at 65 per cent relative humidity. The corresponding figures for Tussah silk are 10.5 and 12.2 per cent. At 61.5 per cent relative humidity, raw silk gave the values 9.81 and 11.18 per cent, and after degumming 8.51 and 9.68 per cent, the data referring to China Filature, 18/20 denier, in which the dry weight of gum was 24 per cent of the dry weight of fibroin. Traces of organic solvents such as alcohol are obstinately retained by silk. Data for moisture regain of natural and artificial silks were summarized by Barker.⁶

PROTEINS

Proteins likewise exhibit a fibrous structure when examined under suitable conditions by X-rays. A suggestion is made by Astbury and Woods⁷ that they consist of extremely long peptide chains—CO—NH—CHR—CO—NH—CHR—which may be arranged singly, in pairs, triads, or a three-fold screw of pairs of chains somewhat similar to the structure of quartz. Speakman and Hirst⁸ point out that the sorption of acid by wool, or presumably by proteins in general, will be accom-

¹ J. Obermiller and M. Goertz, *Melliand Textilber.*, 1926, **7**, 71 (cotton, wool, silk, artificial silks).

² Hönig, *Textilforschung*, Dresden, 1918.

³ H. Sommer, *Melliand Textilber.*, 1928, **9**, 214 (Review, also flax).

⁴ Stolze, *Dissert.*, Marburg, 1914 (Hygrometers).

⁵ Quoted in Silbermann, *Die Seide*, Band II, 190 (Ludwig Degener, Leipzig); and in Vignon and Bay, *La Soie*, 1914, page 145 (Baillièrre et Fils, Paris); source not given.

⁶ S. G. Barker, *Trans. Inst. Chem. Eng.*, 1928, **6**, 166, 167. See also J. Barker and L. P. Priestley, *J. Text. Inst.*, 1925, **16**, 278.

⁷ W. T. Astbury and H. J. Woods, *Nature*, 1931, **127**, 663.

⁸ J. B. Speakman and M. C. Hirst, *Nature*, 1931, **127**, 665.

panied by formation of new surfaces for sorption through simplification of the structure as these chains become separated.

Bancroft and Barnett¹ have recently opened up a new field by studying the amounts of such gases as hydrogen chloride and ammonia which are taken up by different dry proteins at various pressures, using the phase rule as a guide to the existence of definite compounds. Casein, arachin, fibrin, gliadine and adestin form compounds, although zein does not. They all take up ammonia but it is uncertain whether or not chemical combination is responsible.

RUBBER

It is almost impossible to distinguish between persorption and sorption in an extreme case such as that of rubber where there are practically no permanent interspaces within the structural framework such as there are in charcoal. Gases which are sorbed upon particular portions of this framework have to make their own entry much as they must in ordinary solutions, or in massive metals such as palladium or nickel, and just as they have to do in films of collodion that have not already been given porous structure with interspaces of sufficient diameter. This point of view immediately indicates lines of experimental attack, such as measuring the distension of the rubber and the mobility of the persorbed or dissolved molecules (dielectric constant, specific heat, absorption of radiation). For various reasons it has been almost the universal custom to regard gases and vapours as being dissolved in rubber rather than sorbed by it, but no crucial test has yet been made. It is also obvious why cutting rubber into small pieces does not measurably affect the amount of gas sorbed.

Rubber has a definite structure as is evidenced by X-ray examination under appropriate conditions.² The chains of

¹ W. D. Bancroft and C. E. Barnett, *J. Phys. Chem.*, 1930, **34**, 449, 753, 1217, 1930, 2433.

² J. R. Katz, *Kolloid-Z.*, 1925, **36**, 300; J. R. Katz and K. Bing, *Z. angew. Chem.*, 1925, **38**, 545; L. Hock, *Gummi-Ztg.*, 1925, **39**, 1740; *Rubber Age*, 1926, **19**, 141; L. Hock and W. Barth, *Z. physik.*

isoprene, united by primary valencies, form typical helixes which straighten as the rubber is stretched or racked and reveal the essentially fibrous nature of the rubber.

Graham, whilst studying the sorption of gases by palladium and platinum, included experiments on their permeation of rubber.¹ von Wroblewski² found that Henry's law applied to the sorption of hydrogen, air, carbon dioxide and nitric oxide, the amounts increasing in this order and the diffusion constants being one-fiftieth of that in water. Schmidt³ included charcoal, chabasite, metallic powders, various oxides, silicic acid and dehydrated gypsum with rubber amongst the cases to which his sorption and solution formula applied (see Chapter III, page 56). Kanata⁴ also studied the permeabilities of oxygen, hydrogen,⁵ carbon dioxide, sulphur dioxide and ammonia in rubber, gelatine and celluloid.

The sorption of water by rubber was reviewed and carefully studied by Lowry and Kohman.⁶ Henry's law was found to hold up to moderately high relative humidity but increases more rapidly at high humidity and is of course increased by the presence of water soluble components. The rubber was found to increase in volume by an amount equal to the water taken up. The more rigid the rubber, the slower and smaller was the sorption. However, non-hydrocarbons such as proteins are always present in rubber and largely condition the results.

Other vapours were carefully studied by Reiner,⁷ using rubber purified by dissolving in benzene and precipitating

Chem., 1928, **134**, 271 ; P. Bary and E. A. Hauser, *Rev. gén. caoutchouc*, **1928**, No. 42, p. 3 ; *Rubber Age*, 1928, **23**, 685 ; E. A. Hauser, *Ind. Eng. Chem.*, 1929, **21**, 249.

¹ T. Graham, *Chem. Zentr.*, 1867, **38**, 113-120.

² S. von Wroblewski, *Wied. Ann. der Physik*, 1879, **8**, 29.

³ O. Schmidt, *Z. physik. Chem.*, 1928, **133**, 263.

⁴ K. Kanata, *Bull. Chem. Soc. Japan*, 1928, **3**, 183 ; see also A. Dubosc, *Rev. gén. caoutchouc*, 1924, **6**, No. 49, 14.

⁵ For hydrogen sorption see G. Tammann and K. Bochow, *Z. anorg. allgem. Chem.*, 1928, **168**, 322.

⁶ H. H. Lowry and G. T. Kohman, *J. Phys. Chem.*, 1927, **31**, 23. See also J. Barker and L. P. Priestley, *J. Text. Inst.*, 1925, **16**, 282.

⁷ S. Reiner, *Kautschuk*, 1928, **4**, 210.

in alcohol. With such rubber, benzene vapour is slowly but continuously sorbed at 25° C., 0.2 per cent by weight being taken up at one hour, 3.24 per cent at 100 hours, 12.10 per cent at 500 hours and 16.10 per cent at 700 hours when the experiment was discontinued as it promised ultimate complete solution. Wlček¹ had found that rubber took up three times its weight from saturated benzene or one and a half times its weight of benzine.

The sorption of oxygen by rubber has been reviewed and re-studied by Kohman² who finds that it is the essential cause of natural ageing and is different for raw and cured rubber. The number of atoms of oxygen taken up exceeds the number of isoprene units.

The writer is indebted to the Director of Research and to Mr. T. R. Dawson of the Research Association of British Rubber Manufacturers, first for a bibliography³ of all papers in which the absorption or adsorption of gases and water is directly considered in relation to rubber; ⁴ second, for the

¹ Wlček, *Gummi-Ztg.*, 1928, **43**, 310; but see S. Reiner, *Gummi-Ztg.*, 1928, **43**, 370.

² G. T. Kohman, *J. Phys. Chem.*, 1929, **33**, 226.

³ Abbreviations used are *Le Caout.* for *Le Caoutchouc et la Gutta-Percha*, Paris; *G.Z.* for *Gummi-Zeitung*, Berlin; *I.R.J.* for *India Rubber Journal*, London; *Rev. Gén. Caout.* for *Revue Générale du Caoutchouc*, Paris; and *I.R.I. Trans.* for *Institution of the Rubber Industry*, London.

⁴ D. H. Andrews and J. Johnston, *J. Am. Chem. Soc.*, 1924, **46**, 640. E. V. Alekseevski, *Zhur. Prikladnoi Khim.*, 1928, **1**, 184. P. Bary, *Rev. Gén. Caout.*, 1926, Nov., p. 5. C. R. Boggs and J. T. Blake, *Ind. Eng. Chem.*, 1926, **18**, 224-232. Carrier Engineering Corporation Laboratories, *International Critical Tables*, 1927, **2**, p. 324. P. Chappuis, *Ann. Physik*, 1883, **19**, 21. D'Arsonval, *Compt. rend.*, 1899, **128**, 1545. R. Ditmar, *I.R.J.*, 1907, **34**, 85, 197; *Lectures on India Rubber*, p. 207. A. Dubosc, *Le Caout.*, 1923, **20**, 12,009; *Rev. Gén. Caout.*, 1928, Feb., p. 7; *Rev. Gén. Caout.*, 1929, Feb., p. 14. Flusin and Barry, *Compt. rend.*, 1915, **161**, 589. K. Grosheintz, *Bull. Soc. Ind. Mülhouse*, 1896, **73**. A. S. Houghton, *Proc. Phys. Soc.*, 1922, **35**, 39-44. G. Hufner, *Ann. Phys. Chem.*, 1888, **34**, 1. J. Johnston and H. G. Leopold, *J. Phys. Chem.*, 1928, **32**, 876. J. R. Katz, *Ergebnisse der exakten Naturwissenschaften*, 1925, **4**, 154. H. Kayser, *Wied. Ann.*, 1891, **43**, 544. F. Kirchhof, *Koll. Zeits.*, 1924, **35**, 367-74. H. H. Lowry and G. T. Kohman, *J. Phys. Chem.*, 1927,

literature dealing with permeability of raw rubber, that is, rate of diffusion through a film or layer of rubber;¹ and third, for papers on the permeability of vulcanized rubber.² Some classical papers did not definitely indicate whether the rubber was raw or vulcanized, but permeability is similar for both.

31, 23-57. T. M. Rector, *Ind. Eng. Chem.*, 1923, **15**, 1132. S. Reiner, *G.Z.*, 1928, **42**, 2801. S. Reiner and Wlček, *G.Z.*, 1928, **43**, 310, 370. E. E. Schumacher and I. Ferguson, *Ind. Eng. Chem.*, 1929, **21**, 158. P. Stamberger, *Rec. Trav. Chim.*, 1928, **47**, 316; *Koll. Zeit.*, 1928, **45**, 239. F. Steinitzer, *G.Z.*, 1912, **26**, 1626. G. Tammann and K. Bochow, *Z. anorg. Chem.*, 1928, **168**, 322. B. Warren, *J. Soc. Arts.*, 1878, **26**, No. 1313. I. Williams and A. M. Neal, *Ind. Eng. Chem.*, 1930, **22**, 874. S. von Wroblewski, *Ann. Phys. Chem.*, 1879, **8**, 29. T. Yamamoto, *Bull. Inst. Phys. Chem. Res. (Tokyo)*, 1928, **7**, 999; *Abs. section*, **1**, 96. Zulkowsky, (vul'd), *Ber.*, 1872.

¹ Mitchell, *Roy. Inst. J.*, 1831, **2**, 101, 307. A. Reychler, *Bull. Soc. Chem.*, 1893, **9**, 404; *J. Chim. Phys.*, 1910, **8**, 617; *J. Chim. Phys.*, 1910, **8**, 3. C. S. Venable and T. Fuwa, *J. Ind. Eng. Chem.*, 1922, **14**, 139. S. von Wroblewski, *Pogg. Ann.*, 1876, **8**, 539.

² D. Alexejew and V. Matalski, *J. Chim. Phys.*, 1927, **24**, 737. Aronstein and Sirks, *Jahresber. über die Fortschritte der Chemie*, 1866, p. 54. G. Austerweil, *Compt. rend.*, 1912, **154**, 196; *Die angewandte Chemie in der Luftfahrt.*, 1914. G. Barr, *Rubber Industry*, 1914, p. 265; *Adv. Committee Aero., Technical Repts.*, 1915-16, p. 497; 1916-17, p. 541; 1918-19, p. 1300; *Dictionary of Applied Physics*, 1923, **5**, p. 135; G. Barr and J. Thomas, *Adv. Committee Aero., Technical Repts.*, 1911-12, p. 197; 1912-13, p. 270. Cagniard-Latour, *J. Frank. Inst.*, 1839, **24**, 117. C. de F. Chamdler, *Free and Captive Balloons*, N.Y., 1926, Pt. III, chap. 18, p. 289. W. C. Davey and T. Ohya, *I.R.I. Trans.*, 1929, **5**, 27. H. A. Daynes, *Proc. Roy. Soc.*, 1920 (A), **97**, 286; *I.R.I. Trans.*, 1928, **3**, 428. D. De Prat, *Tissus Imperméables*, Paris, 1913, p. 129. J. Dewar, *Proc. Roy. Inst.*, 1918, **21**, 558, 813. J. W. W. Dyer, *Aeronautical J.*, 1921, **25**, 332. J. D. Edwards, *U.S. Bureau of Standards, Tech. Paper* 113, 1918. J. D. Edwards and S. F. Pickering, *U.S. Bureau of Standards, Sci. Paper* 387, 1920. A. C. Fieldner, S. H. Katz and S. F. Kinney, *U.S. Bureau of Mines, Tech. Paper* 272, 1921. W. Frenzel, *Über die Gasdurchlässigkeit der gummierten Ballonstoffe*, Gebweiler, 1912; *Chem. Zeit.*, 1919, **43**, 530. Gibbons and Smith, *Permeability of Balloon Fabrics. First Ann. Rep. of N.A.C.A.*, Washington, 1915. T. Graham, *Phil. Trans.*, 1866, **156**, 399. L. Grunmach, *Phys. Zeit.*, 1905, **6**, 795. O. Hackl, *Chem. Ztg.*, 1927, **51**, 993. Hempel, *Ber.*, 1882, **15**, 912. V. Henri, *Le*

VARIOUS MATERIALS

As an approximate guide to the hygroscopic properties of a great variety of materials the data of Wilson and Fuwa¹ may be quoted in tables 49 and 50.

TABLE 49

Classification of Materials into Four Groups according to the Number of grams of Water sorbed per 100 gms. of Dry Weight at 50 per cent and 90 per cent Relative Humidity

0 to 4 and 0 to 6 . . .	Finely divided inorganic substances, carbon and lampblacks, coke, rubber, cellulose acetate silk
4 to 8 and 8 to 19 . . .	Foodstuffs (except macaroni), paper and pulp fibres, glue, fuller's earth, linen
8 to 12 and 13 to 26 . . .	Artificial and natural textile fibres (except cellulose acetate), macaroni, feathers, wood, soap, catgut, ferric hydroxide gel
12 to 28 and 22 to 50 . . .	Absorbent cotton, leather, cigarette tobacco, silica gel, activated charcoal

Caout., 1910, **7**, 4351. Heyn, *Preuss. Akad. Wiss. Berlin Ber.*, 1911, **14**, 365. S. E. Hill, *Science*, 1928, Apr. 6th, p. 374. Josse, *L'Aéro-phile*, 1910, p. 156. K. Kanata, *Bull. Chem. Soc. Japan*, 1928, **3**, 183. Kobbe, *Thonind. Zeit.*, 1890, **14**, 297. P. Masucci and M. I. Moffat, *J. Am. Pharm. Assoc.*, 1923, **12**, 117-20. V. N. Morris and J. N. Street, *Ind. Eng. Chem.*, 1929, **21**, 1215. Payen, *Compt. rend.*, 1852, **36**, 3; 1852, **37**, 453; 1866, **63**, 533; 1871, **72**, 148. Peyron, *Compt. rend.*, 1841, **13**, 820. B. D. Porritt and W. S. Allen, *Adv. Committee for Aero., Technical Rept.*, 1917-18, p. 1100. Rayleigh, *Phil. Mag.*, 1900, **49**, 220. A. D. Ritchie, *Adv. Committee Aero., Technical Rept.*, 1918-19, p. 1316. O. Rodt, *Chem. Zeit.*, 1914, **38**, 1249. W. Rosenhain and G. Barr, *Adv. Committee Aero., Technical Rept.*, 1909-10, p. 86. W. Rosenhain, G. Barr and H. Booth, *Adv. Committee Aero., Technical Rept.*, 1910-11, pp. 57, 65. E. E. Schumacher and I. Ferguson, *J. Amer. Chem. Soc.*, 1927, **49**, 427. G. A. Shakespear, *Adv. Committee Aero., Technical Rept.*, 1916-17, p. 579; 1917-18, pp. 1080, 1087; 1918-19, p. 1386; G. A. Shakespear and H. A. Daynes, *Adv. Committee Aero., Technical Rept.*, 1917-18, p. 1103; *Proc. Roy. Soc.*, 1920 (A), **97**, 273. G. A. Shakespear, H. A. Daynes and L. J. Lambourn, *Adv. Committee Aero., Technical Rept.*, 1918-19, p. 1380. H. I. Terry, *G.Z.*, 1897, **12**, 22. A. J. Wineland and R. N. Waters, *Anesthesia and Analgesia*, 1929, **8**, 322. Anon., *G.Z.*, 1926, **40**, 1881.

¹ R. E. Wilson and T. Fuwa, *J. Ind. Eng. Chem.*, 1922, **14**, 915.

TABLE 50

The Sorption of Moisture by Various Materials at Certain Relative Humidities

Substance	Per cent of water on dry basis Per cent relative humidity				
	15	30	50	70	90
<i>Group 1.—Natural Textile Fibres</i>					
Sterile absorbent cotton . . .	8.0	10.1	20.6	22.2	25.8
Cotton sheeting . . .	2.99	4.56	6.7	9.6	13.5
Table-linen material . . .	2.53	3.60	5.1	7.0	10.2
Average several grades of jute .	4.33	6.9	10.2	14.4	20.2
Worsted (wool) . . .	6.3	9.0	12.2	17.0	22.9
Raw silk (Cheyennes) . . .	5.0	7.1	9.0	13.3	19.0
Strands from Sisal hemp rope .	4.48	5.6	8.3	11.7	15.1
Strands from Manila hemp rope .	4.25	5.6	8.5	11.7	16.0
<i>Group 2.—Artificial Textile Fibres</i>					
White viscose silk . . .	5.6	6.7	9.4	12.9	16.8
Red viscose silk . . .	5.3	6.4	9.0	11.8	15.2
Nitrocellulose silk . . .	3.95	7.0	9.1	11.8	16.0
Cellulose acetate silk . . .	0.97	1.43	2.44	3.56	5.26
<i>Group 3.—Paper and Pulp Fibres</i>					
Mechanical pulp (pine) . . .	4.55	6.3	7.9	9.5	12.0
Sulphite cellulose pulp . . .	3.35	5.8	6.3	7.8	10.5
Soda cellulose pulp . . .	3.49	5.0	6.6	8.0	10.2
Kraft paper . . .	2.50	3.85	5.4	7.0	9.2
Bond paper . . .	2.34	3.71	5.1	6.5	8.1
Filter paper (quantitative) . .	2.51	4.21	5.6	7.4	10.1
Cornell wall board . . .	3.71	5.3	7.5	10.3	13.0
				(at 80%)	
<i>Group 4.—Foodstuffs</i>					
White bread . . .	0.99	3.14	6.2	11.0	19.0
Crackers ("Uneda" Biscuit) .	2.51	3.32	4.98	8.3	14.9
Macaroni . . .	6.5	8.8	11.7	16.2	22.1
Flour . . .	3.55	5.3	7.9	12.3	19.1
Starch . . .	2.83	5.4	7.6	8.9	12.7
Gelatin . . .	1.01	2.80	4.92	7.6	11.4
<i>Group 5.—Other Organic Colloids</i>					
Leather (sole) . . .	7.0	11.1	16.0	20.6	29.2
Catgut (from racquet strings) .	6.2	8.6	12.0	17.3	21.7
Glue (best grade hide) . . .	4.24	5.8	7.6	10.7	12.5
Feathers (pillow down) . . .	5.0	6.4	8.1	10.4	12.7
Rubber (Goodyear solid tyre) .	0.17	0.28	0.60	0.74	0.99
Wood (timber, average) . . .	4.65	6.9	9.0	11.5	18.6
Soap (Ivory) . . .	3.36	4.62	8.4	18.4	23.8
Tobacco (Fatima cigarettes) .	8.9	10.1	16.0	24.5	50.1

Group 6.—Absorbents of Various Kinds

Carbon black	2.48	3.42	3.85	4.31	6.0
Ferric hydroxide gel . .	5.2	6.8	8.1	12.6	20.0
Silica gel	8.0	12.7	17.3	20.2	22.6
Soda lime	2.0	3.5	6.5	11.6	24.0
Steam activated coconut charcoal	9.5	22.8	28.3	30.0	32.7
Fuller's earth (Florida clay) .	4.54	—	7.5	—	15.6

Group 7.—Various Forms of Carbon

Domestic coke	0.33	0.60	1.02	1.48	1.89
Carbon black	2.48	3.42	3.85	4.31	6.0
Steam activated coconut charcoal	9.5	22.8	28.3	30.0	32.7

Group 8.—Finely Divided Inorganic Substances

Asbestos fibre	0.22	0.26	0.40	0.62	0.84
Kieselguhr ("Celite") . .	0.50	0.88	1.40	2.00	3.19
Zinc oxide	0.17	0.29	0.36	0.41	0.59
Kaolin (Florida)	0.30	0.60	0.92	1.06	1.27
Glass wool	0.09	0.09	0.17	0.23	0.40

CHAPTER XIII

THE EFFECT OF SORPTION UPON THE SOLID

DISTENSION OF CHARCOAL CAUSED BY SORPTION

It is commonly taken for granted that when a rigid body such as charcoal, zeolite or a metal sorbs a gas, there is little or no effect upon the properties of the solid itself. The swelling of the so-called non-rigid jellies such as cellulose derivatives, wool or rubber is not usually discussed in connexion with the subject of sorption.¹ It comes therefore as a surprise to most investigators to find that the dimensions of a metal, a crystal or a rigid porous body undergo an appreciable increase during the processes of sorption. The phenomena differ perhaps more in degree than in kind from those involved in the swelling of jellies.²

The swelling of charcoal during the sorption of carbon dioxide was looked for in connexion with a discussion of the phenomena involved in the disintegration of building materials. It had been found that building materials expand slightly during the sorption of water,³ and this is accompanied by a fundamental change in physical properties. The expansion of charcoal is of the same order. Meehan⁴ placed a 3-in. cube of charcoal prepared from yellow pine in an extensometer surrounded by a vessel which could be evacuated. Upon introduction of one atmosphere of carbon dioxide the linear expansion was about 0.25 per cent at 10° C., 0.22 per cent at 16.4° C., and 0.11 per cent at 35.8° C., independent

¹ Compare Chapter V, page 167, footnote 2.

² For references to the effect of opening up of space lattices upon reactivity, see J. A. Hedvall, *Z. Elektrochem.*, 1930, **36**, 853.

³ Compare J. W. McBain and J. Ferguson, *J. Phys. Chem.*, 1927, **31**, 564.

⁴ F. T. Meehan, *Proc. Roy. Soc. (London)*, A, 1927, **115**, 199.

of the direction of the grain. This corresponds to volume expansions of 0.75 per cent, 0.66 per cent, and 0.33 per cent per atmosphere of carbon dioxide. At temperatures between 15° C. and 35.8° C. the expansion increased more than in proportion to the pressure of carbon dioxide. As the carbon dioxide was removed, the charcoal resumed its original dimensions. The observations are summarized in the equation, $1/E = 1.59 + 0.885(100/p)(t + 6.5)$, where E is the linear expansion in per cent, p the pressure of carbon dioxide in millimetres of mercury, and t the temperature in degrees centigrade.

J. L. Porter in the writer's laboratory has observed and measured the expansion when charcoal is exposed to the vapours of organic liquids. His parallel observation of water on charcoal is of decisive theoretical importance in that it disproves the hypothesis that water is taken up by charcoal by capillary condensation (see Chapter IV, page 148).

The results of Meehan were confirmed and extended by Bangham and Fakhoury.¹ Their results with four vapours at 18°–20° C. are given in table 51. It will be noticed that for a given weight sorbed, the expansion increases in the order sulphur dioxide, water, carbon dioxide and ammonia.

TABLE 51

Linear Expansion of Willow Charcoal (in per cent) caused by Sorption (in grams per gram of Charcoal)

Sulphur dioxide		Water		Carbon dioxide		Ammonia	
x/m .	Per cent	x/m	Per cent	x/m	Per cent	x/m	Per cent
0.022	0.023	0.008	0.018	0.014	0.016	0.010	0.026
0.050	0.052	0.025	0.035	0.029	0.038	0.016	0.042
0.078	0.096	0.048	0.058	0.051	0.081	0.023	0.064
0.102	0.162	0.068	0.094	0.058	0.102	0.038	0.128
0.138	0.329	0.078	0.122	0.065	0.123	0.045	0.171
0.142	0.361	0.091	0.170	0.068	0.137	0.051	0.212
0.149	0.414	0.107	0.238	0.073	0.158	0.061	0.303
0.152	0.448	—	—	—	—	0.065	0.354
0.153	0.461	—	—	—	—	0.071	0.427

¹ D. H. Bangham and N. Fakhoury, *Nature*, 1928, **122**, 681; corrected and extended in *Proc. Roy. Soc. (London)*, A, 1930, **130**, 81.

Bangham¹ concludes that "Those atomic groups which have entered into combination with gas molecules are in a configuration different from the remainder and the change they have undergone imposes a stress on the rigid framework which surrounds them." The activity of active sorbents "may be almost completely masked, however, when the units are rigidly bound together; a parallel behaviour is shown by those metallic oxides which, by high-temperature ignition, are made to lose their power of re-hydration," at least in a reasonable time. "The sorbed molecules are regarded as distending the rigidly cohering structure of the sorbent, which consequently becomes stressed. This distension may occur even if the structure is a sufficiently open one to permit easy penetration by the gas molecules in their free state."

OTHER RELATED EFFECTS WITH VARIOUS SOLIDS

Bangham correlates in an interesting way the time relations of sorption with other changes taking place in the solid phase which exhibit similar time laws, such as photoelectric fatigue, variation of capacities of lead accumulators during charging, resistance of selenium on exposure to light, deformation of solids of widely different type under steady load, the behaviour of dielectrics during charge and discharge, the change in X-ray structure of rubber under constant tension, the change of volume accompanying ionic exchange and variation of water content of the zeolites,² and Smits' conception of "pseudo-binary" systems.

These effects with charcoal are closely related to a phenomenon studied by Pavlov³ who merely noted the change in apparent volume of powdered charcoal placed in a test tube when submerged under various liquids and solutions. Similar increases of from 7 to 13 per cent in the height in a test tube have been observed with silica gels immersed in benzene

¹ D. H. Bangham, *Phil. Mag.*, (7), 1928, **5**, 737.

² G. Schulze, *Z. physik. Chem.*, 1914, **89**, 168.

³ P. N. Pavlov, *Kolloid-Z.*, 1927, **42**, 112.

solutions of acetic acid.¹ Ostwald and Haller² in similar experiments with powdered talc, fuller's earth, alumina, silica, magnesia, calcium carbonate, ferric oxide, graphite and carbon found that the volume of the sediment was greatest in carbon tetrachloride, decreasing in the order hexane, benzene, chloroform, ether, acetic acid, alcohol, and acetone, and was decreased by de-gassing the powders or lowering the temperature.

Some bentonites swell in water to the very large extent of 13.8 fold without losing coherence.³ According to Spence,⁴ thorough drying in the air or addition of a few per cent of electrolyte to the water diminishes the amount of swelling.

Other properties than the mere dimensions of charcoal are affected. Thus its electrical resistance⁵ is slightly increased by exposure to air or, still more, ammonia. The change increases with pressure.

The effects here discussed may or may not be inherently related to the influence of sorbed water on the electrical conductivity of powders as studied by Kenrick and Giffen.⁶ Some powders, like glass, conducted well even with small concentrations of water vapour; others, like silicic acid, remained practically non-conducting until the saturation point was reached, when all powders conducted well.

EXAMPLES OF DISINTEGRATION AND SWELLING CAUSED BY SORPTION

The local expansion caused by sorption is readily demonstrated. For example, Zsigmondy⁷ states that the trans-

¹ E. Bosshard and E. Jaag, *Helv. Chim. Acta*, 1929, **12**, 105. For another form of swelling experiment with various powders, see H. Freundlich and W. Sachs, *Z. physik. Chem.*, Abt. A, 1929, **145**, 177.

² W. Ostwald and W. Haller, *Kolloidchem. Beihefte*, 1929, **29**, 354.

³ J. H. Frydlander, *Rev. prod. chim.*, 1929, **32**, 325, 357. Practical directions for such experiments are given by C. W. Davis and H. C. Vacher, *U.S. Bur. Mines*, Tech. Paper, 1928, No. 438.

⁴ H. S. Spence, *Can. Dept. Mines*, Mines Branch, 1924, No. 626.

⁵ K. Siebel, *Z. Physik*, 1921, **4**, 288.

⁶ F. B. Kenrick and F. J. Giffen, *Colloid Symposium Monograph* (Toronto, 1928), 1928, **6**, 53; see also Chapter VII, page 218.

⁷ R. Zsigmondy, *Z. anorg. Chem.*, 1911, **71**, 356; earlier references are cited there.

parent, glass-like jelly of silica, either of natural origin such as the tabaschir occurring in bamboo or that artificially prepared, if dry, when thrown into water bursts or disintegrates with the sudden strains set up locally. Similarly, Bosshard and Jaag¹ noted that silica gel, when thrown into water, alcohol, "and other liquids, particularly those of high surface tension," generally bursts with audible decrepitation. Likewise, J. L. Porter in the author's laboratory finds that dehydrated chabasite is completely disintegrated by too rapid exposure to water. It seems to us that much of the well known roughening or even disintegration of catalysts may be attributable to this cause.²

Miss Schirmann³ shows interesting microphotographs of the surface and interior of a palladium wire "activated", or given a porous structure, by repeated heating and cooling in an atmosphere of varying pressure, and subsequently freed from gas by extreme evacuation or by ion bombardment in a discharge tube without electrodes. She used platinum, palladium and silver in this state. Similar activation may be brought about by intermittent exposure to gas at 25 atmospheres pressure. Miss Schirmann explores with these materials the novel field which she entitles "thermal molecular sorption". It is based upon the Knudsen effect, $p_1/p_2 = \sqrt{T_2/T_1}$, where the diameter A of the pores is of the order of, or smaller than, the free path λ of the molecules. This movement of the gas is initiated by surface cooling, whereupon the amount of gas taken up depends on the temperature gradient and on A/λ , but is little affected by the gas pressure. The gas sorbed on the interior of the pores of palladium amounted to several hundred times the volume of the metal and was the same for argon, neon, helium and nitrogen. Hydrogen was taken up to the extent of 1,500 volumes by palladium, owing to permeation of the space lattice.

¹ E. Bosshard and E. Jaag, *Helv. Chim. Acta*, 1929, **12**, 105.

² Compare Chapter XVIII; see also the reference to Berliner, Chapter IX, page 264, upon the disintegration of metals during desorption.

³ M. A. Schirmann, *Z. tech. Physik*, 1929, **10**, 640.

Gurwitsch¹ found that sorptive forces can cause spontaneous pulverization. He found that many liquids have this action upon floridin; and with some mechanical assistance he found that the same liquids, such as water and methyl alcohol, can reduce metals (lead, cadmium, zinc and bismuth, mercury and tin) to a fine powder or even a colloidal state. A small amount of such an active liquid is able to exert a considerable effect when dissolved in an indifferent liquid.

The contraction of the typical zeolite, analcite, upon dehydration was followed by Friedel.² It is linear during the loss of the first 7 per cent of water and amounts to 1 per cent by volume up to this point, but it rises to 2 per cent by volume for the loss of 1 more per cent of water.

van Bemmelen³ was unable to measure the expansion or contraction of specimens of silicic acid, some fresh, some five years old, when once they had been dehydrated as far as the point *O*,⁴ but surmised that thereafter there was a slight contraction on hydration and expansion on dehydration. He refers to the more definite and striking finding of Rodewald⁵ that a starch preparation dried over sulphuric acid contracts upon imbibing water up to 31 per cent and expands again upon losing this water. The expansion amounted to 7.3 per cent when the air dried preparation lost 16.33 per cent by weight of water. It would appear that these observations of Rodewald and van Bemmelen are not due to sorption but to the compression caused by surface tension of the liquid in the open pores in accordance with the interpretation of Zsigmondy and Bachmann.⁶ The latter made measurements on gelatine gels in various liquids. Reference may, however,

¹ L. G. Gurwitsch, *J. Russ. Phys.-Chem. Soc.*, 1916, **48**, 856.

² G. Friedel, *Bull. soc. franc. minéral.*, 1896, **19**, 381. Expansion of a space lattice may occur during base exchange (W. Eitel, E. Herlinger and G. Trömel, *Naturwissenschaften*, 1930, **18**, 469).

³ J. M. van Bemmelen, *Die Absorption*, 1910, p. 339; *Z. anorg. Chem.*, 1898, **18**, 98.

⁴ See Chapter VI, page 183.

⁵ H. Rodewald, *Z. physik. Chem.*, 1897, **24**, 193.

⁶ W. Bachmann, *Z. anorg. allgem. Chem.*, 1917, **100**, 45.

be made to the demonstration by Speakman¹ that methyl alcohol or ethylene glycol may enter wool fibres, causing them to swell and open the pores until they are able to admit larger molecules such as normal propyl alcohol.

EFFECT OF GASES UPON THE PROPERTIES OF IRON AND PLATINUM

Like charcoal, metals swell and change their electrical conductivity when sorption occurs.² Thus iron which has been used as a cathode in electrolysis increases³ in electrical resistance as do also tantalum, palladium and crystalline platinum which sorbs comparatively little hydrogen and shows merely a decrease in resistance, which, after interruption of the electrolysis, is slowly restored. An iron cathode is temporarily embrittled.⁴ The same is true of iron that has stood in contact with acids⁵ or an iron wire that has been heated above 900° C. in hydrogen and quickly chilled so that it retains about 0.16 volumes (at N.T.P.) of hydrogen, which gradually escapes.⁶

Granular and crystalline fractures may often be attributable to gaseous movements within the amorphous intergranular cement as, for example, during tempering operations. This may result in recrystallization.

The increase in tensile properties of iron and its decrease in length when it takes up nitrogen from an atmosphere of nitrogen or ammonia are ascribed to the formation of nitride of iron which may completely suppress all the critical points.⁷

¹ J. B. Speakman, *Nature*, 1930, **126**, 565.

² A. W. Gauger (*J. Am. Chem. Soc.*, 1925, **47**, 2323) was unable to obtain reproducible results with a platinum film on glass exposed to nitrogen and hydrogen, owing to its colloidal nature.

³ E. A. Harding and D. P. Smith, *J. Am. Chem. Soc.*, 1918, **40**, 1529.

⁴ J. H. Andrew, *Trans. Farad. Soc.*, 1919, **14**, 232.

⁵ E. Heyn, *Stahl und Eisen*, 1900, **20**, 837.

⁶ A. Sieverts, *Z. Metallkunde*, 1929, **21**, 40.

⁷ J. H. Andrew, *Trans. Farad. Soc.*, 1919, **14**, 232; *J. Iron and Steel Inst.*, 1912, **86**, No. 2, 210; N. Tschischewski, *J. Iron and Steel Inst.*, 1915, **92**, No. 2, 47.

The space lattice of platinum expands in each direction by 2.4, 2.8, and 2.9 per cent when it sorbs hydrogen, carbon monoxide, and oxygen, respectively.¹ When the large diameter of the last two molecules is recalled, it is evident that diffusion is not easy and is accompanied by great local strain, additional to that caused by the presence of the final expanded lattice.

EFFECT OF HYDROGEN UPON THE DIMENSIONS AND CONDUCTIVITY OF PALLADIUM

The most extensively studied system is hydrogen-palladium. Graham,² the discoverer of the now discredited compound Pd_2H , found that palladium wire lengthened by about 5 per cent when it took up hydrogen. Upon removal of the hydrogen, the wire shortened below its original length until, after some repetitions, it was 15 per cent shorter than at first. Thereafter its sorptive power was greatly impaired and the wire tended to disintegrate. Wires of palladium alloyed with platinum, silver and gold lengthened about twice as much as those of pure palladium. Poggendorff³ devised a striking demonstration of the expansion. Dewar⁴ has also devised a simple but very striking and instructive lecture experiment to demonstrate the rapidity of sorption and desorption of hydrogen by palladium, the expansion and contraction caused thereby, and the effect of heat. Thoma⁵ found that an electrolytically charged wire increased in length, as well as in diameter, by 3.8 per cent.

Fischer⁶ found the expansion to be proportional to the

¹ A. Osawa, *Science Repts. Tôhoku Imp. Univ.*, (1), 1925, **14**, 45.

² T. Graham, *J. Chem. Soc.*, 1869, **22**, 419; *Proc. Roy. Soc. Edin.*, 1869, **6**, 504; *Proc. Roy. Soc. (London)*, 1869, **17**, 212, 500; *Compt. rend.*, 1869, **68**, 101, 1511; *Chem. News*, 1869, **19**, 52; 1869, **20**, 16; *Pogg. Ann. der Physik*, 1869, **136**, 317; 1869, **138**, 49.

³ J. C. Poggendorff, *Phil. Mag.*, (4), 1869, **37**, 474.

⁴ J. Dewar, *Trans. Roy. Soc. Edin.*, 1876, **27**, 173.

⁵ M. Thoma, *Z. physik. Chem.*, 1889, **3**, 71. Platinum, nickel, iron and aluminium may likewise be charged with hydrogen to a certain extent when used as cathodes in electrolysis, but the iron and platinum show no change in volume thereby.

⁶ F. Fischer, *Ann. der Physik*, (4), 1906, **20**, 40.

amount of hydrogen sorbed up to 1,000 volumes and thereafter to increase more rapidly.

The expansion of the space lattice of palladium already referred to in Chapter IX, page 302, is found to be 2.8 per cent by Yamada¹ and Osawa,² direct measurement of the diameter of a 0.5 mm. wire giving 2.9 per cent when 660 volumes of hydrogen were sorbed at room temperature and pressure. The expansion found by McKeehan³ was 3.5 per cent, while Krüger and Sacklowski⁴ introduced only enough hydrogen to obtain 2.3 per cent.⁵

Careful measurements of the diameter and length of palladium wires, originally 0.5 and 0.77 mm. in diameter, were made by Wolf.⁶ The first amount of hydrogen was quickly taken up when the wire was used as a cathode, but the greater part required much time and excess pressure. The expansion of the wire varies hyperbolically during the sorption of the first 100 volumes of hydrogen and is thereafter in linear proportion up to the final 823 or 847 volumes. The length of these two wires increased by 3.19 per cent and 0.77 per cent, respectively, whereas their diameters increased by 6.78 per cent and 6.12 per cent. The wire did not shrink when all but 250 volumes had been removed by a 14-day evacuation at room temperature, but after the remainder was removed by heating, the wire resumed its original dimensions. Harding and Smith⁷ observed fluctuations or discontinuities in the

¹ M. Yamada, *Phil. Mag.*, (6), 1923, **45**, 241; *Science Repts. Tōhoku Imp. Univ.*, (1), 1922, **11**, 451.

² A. Osawa, *Science Repts. Tōhoku Imp. Univ.*, (1), 1925, **14**, 45.

³ L. W. McKeehan, *Phys. Rev.*, (2), 1923, **21**, 334; 1922, **20**, 82.

⁴ F. Krüger and A. Sacklowski, *Ann. der Physik*, (4), 1925, **78**, 72.

⁵ This may be compared with the increase of 6 per cent in lattice spacing found for nickel sputtered in hydrogen as compared with pure nickel (L. R. Ingersoll, *J. Am. Chem. Soc.*, 1931, **53**, 2008).

⁶ G. Wolf, *Z. physik. Chem.*, 1914, **87**, 575.

⁷ E. A. Harding and D. P. Smith, *J. Am. Chem. Soc.*, 1918, **40**, 1508; for a discussion of the interpretation of their observations in regard to changes in length and electrical resistance, see E. Newbery, *J. Am. Chem. Soc.*, 1919, **41**, 1887, 1895; E. A. Harding and D. P. Smith, *J. Am. Chem. Soc.*, 1919, **41**, 1892, 1897.

change in length of a fine palladium wire during the charge and discharge of hydrogen.

The electrical resistance of palladium increases greatly as hydrogen is sorbed,¹ rising to more than double the original value. The increase is approximately a linear function of hydrogen taken up.² There is a greater increase for the first 40 volumes taken up from an atmosphere of hydrogen followed by a slower, not quite linear increase from there up to 600 volumes. Thereafter the increase is linear according to Wolf,³ but with a slight maximum at the composition $\text{Pd} + 0.75\text{H}$ according to Linde and Borelius,⁴ or a constant resistance above 1,000 volumes according to Fischer.⁵

Sorption of gases may be studied through the skin effect upon electrical conductivity for high frequency alternating currents only, as in the case of platinum wires upon which nitrogen and carbon dioxide are sorbed, direct current being unaffected. Hydrogen, on the other hand, alters both kinds of current and this is interpreted by Dobretsberger⁶ as adsorption plus absorption.

¹ Becker, published by T. Graham, *Proc. Roy. Soc. (London)*, 1869, **17**, 212; *J. Chem. Soc.*, 1869, **22**, 419; *Compt. rend.*, 1869, **68**, 101; *Chem. News*, 1869, **19**, 52; *Pogg. Ann. der Physik*, 1869, **136**, 317. See also, C. G. Knott, *Proc. Roy. Soc. Edin.*, 1883, **12**, 181; *Trans. Roy. Soc. Edin.*, 1888, **33**, 171; A. Krakau, *Z. phys. Chem.*, 1895, **17**, 689.

² W. E. McElfresh, *Proc. Am. Acad. Arts Sci.*, 1904, **39**, 323; F. Fischer, *Ann. der Physik*, (4), 1906, **20**, 503. A. Sieverts, *Intern. Z. Metallog.*, 1913, **3**, 37 (the resistance of platinum, copper, iron and nickel is not affected by an atmosphere of hydrogen up to 920°C., nor does carbon monoxide affect that of nickel).

³ G. Wolf, *Z. physik. Chem.*, 1914, **87**, 575.

⁴ J. O. Linde and G. Borelius, *Ann. der Physik*, (4), 1927, **84**, 747.

⁵ F. Fischer, *Ann. der Physik*, (4), 1906, **20**, 503.

⁶ H. Dobretsberger, *Z. Physik*, 1930, **65**, 334.

CHAPTER XIV

HEAT OF SORPTION

METHOD OF MEASUREMENT

One of the significant quantities connected with sorption is the evolution of heat. It is of interest to know its exact value and the way it varies with the amount of sorption as well as to compare it with such quantities as latent heats of vaporization and typical heats of reaction. It has found application in the production of low temperatures, as, for example, reaching 6° abs. by pumping off hydrogen sorbed at the temperature of liquid air or liquid hydrogen.¹

Heat of sorption is usually and most simply obtained by comparison of two isotherms. Comparing the pressures at two temperatures corresponding to any one fixed value of x/m , that is, two points on the same isostere, the heat of sorption follows from the equation, $d \ln p/dT = -q/RT^2$. This value of q refers to the differential or instantaneous heat for the addition of further small amounts to a surface by which x has already been sorbed, as distinguished from the integral heat of sorption where x is the total amount sorbed by the quantity m of sorbing material. q is the molar heat in each case, that is, the number of small calories per gram molecular weight of the gas or vapour sorbed.² Heat of sorption so

¹ F. Simon, *Physik. Z.*, 1926, **27**, 790; P. Mautner, *Kolloid-Z.*, 1927, **42**, 275; see also D. H. Andrews, R. K. Witt and E. Crigler (*Refrigerating Eng.*, 1930, **19**, 177) who used hydrogen, carbon monoxide and ethylene.

² For the restrictions upon the validity of this formula and its complete inapplicability to certain cases, see the writer's conception of steric hindrance in Chapter IV, page 141. For a more complete expansion of the terms involved see H. R. Kruyt and J. G. Modderman (*Chemical Reviews*, 1930, **7**, 280); in taking into account the effect

calculated is less trustworthy than that directly measured unless it is known that the amount of impurities and the extent to which they are displaced during sorption are independent of the temperature.

Coolidge ¹ has shown that heats of sorption calculated from isosteres have, as a matter of fact, a tendency to be somewhat less than those directly measured. A further illustration is found in the data of Pearce and Johnstone ² who quote the following values calculated from isosteres of vapours with activated charcoal, all somewhat lower than the corresponding measured values: ³ methane 3,750, methyl chloride 8,300, carbon tetrachloride 8,900, dichlormethane, 10,450, and chloroform 10,700 calories.

Heat of sorption is directly measured by means of a calorimeter. Usually an ice calorimeter is employed on account of its advantages of accuracy and its ability to measure heat which may only slowly become available from poorly conducting porous materials.⁴ Fig. 121 (Lamb and Coolidge)⁵ and

of the constraint within the solid here discussed, the next to the last term in their equation 5 could not be considered as negligible. On pages 283 and 284 (*loc. cit.*) they list further experimental influences which may occasion disagreement between theoretical and experimental values for heat of sorption. 1. Langmuir and K. H. Kingdon (*Proc. Roy. Soc. (London)*, A, 1925, **107**, 71) use this formula to calculate the heat of desorption of positive caesium ions from a surface of tungsten; and I. Langmuir and D. S. Villars (*J. Am. Chem. Soc.*, 1931, **53**, 486) for the heat of desorption of oxygen from tungsten; namely, 162,000 calories per gram atom.

¹ A. S. Coolidge, *J. Am. Chem. Soc.*, 1926, **48**, 1806; see also J. N. Pearce and A. L. Taylor, *J. Phys. Chem.*, 1931, **35**, 1099.

² J. N. Pearce and H. F. Johnstone, *J. Phys. Chem.*, 1930, **34**, 1274.

³ J. N. Pearce and L. McKinley, *J. Phys. Chem.*, 1928, **32**, 368; see this chapter, page 407; L. McKinley and J. N. Pearce, *Proc. Acad. Sci.*, 1927, **34**, 216; L. McKinley, *Dissert.*, State University of Iowa, 1927.

⁴ At 40° S. J. Gregg used a phenol calorimeter for comparison with the results obtained by the ice calorimeter at 0° (*J. Chem. Soc.*, **1927**, 1494).

⁵ A. B. Lamb and A. S. Coolidge, *J. Am. Chem. Soc.*, 1920, **42**, 1147, fig. 1.

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fig. 122 (Marshall and Bramston-Cook)¹ show suitable modern forms of this apparatus. Dewar,² fig. 123, utilized a liquid air calorimeter at -185°C . where the heat evolved on admitting gas to the charcoal was measured by the amount of liquid air evaporated from an insulated container surrounding the latter.

Several investigators have employed thermocouples em-

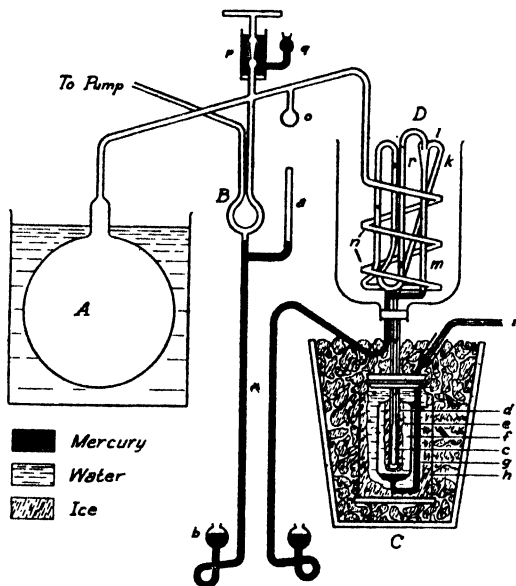


Fig. 121.—Sorption Apparatus of Lamb and Coolidge with Ice Calorimeter C.

bedded in the sorbing material, deducing the heat of sorption from the rise in temperature of the material itself. Thus Chattock determines relative humidity in any confined space, such as that under the wing of an incubating hen, with a thermocouple whose end is wrapped with a wisp of dried cotton. The most careful measurements of this sort are those

¹ M. J. Marshall and H. E. Bramston-Cook, *J. Am. Chem. Soc.*, 1929, **51**, 2020, fig. 1.

² J. Dewar, *Proc. Roy. Soc. (London)*, 1904, **74**, 124.

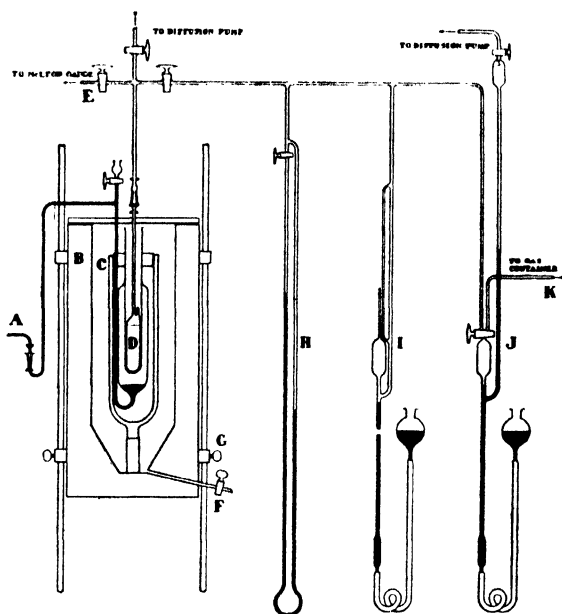


Fig. 122.—Sorption Apparatus of Marshall and Bramston-Cook with Ice Calorimeter C.

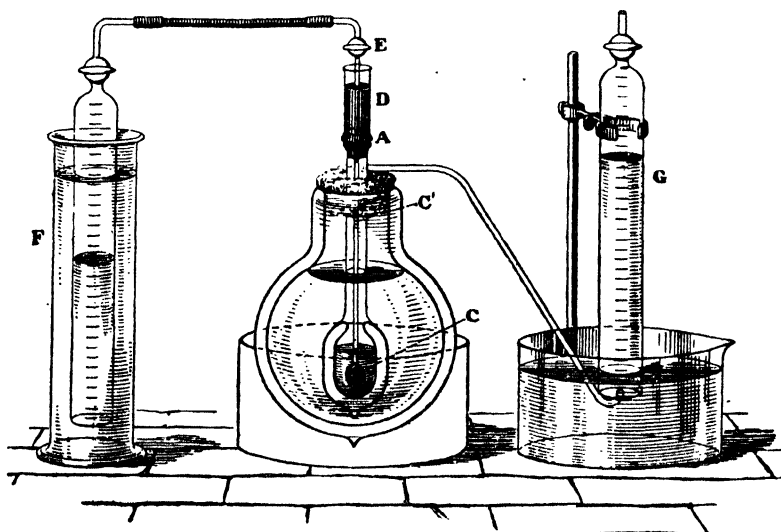


Fig. 123.—Sorption Apparatus of Dewar with Liquid Air Calorimeter.

0°C., fig. 124, similar to that commonly used in the study of specific heats at low temperatures.

TYPICAL HEATS OF SORPTION

Turning to numerical results, those of Chappuis,¹ obtained in 1883 for the heat of sorption of ammonia on meerschaum at 0°, are typical. The molar heat q was 20,500 calories at the lowest pressures, that is, for initial sorption, falling to 7,600 calories as the sorption proceeded and the pressure rose to nearly one atmosphere. These numbers should be compared with the latent heat of condensation of ammonia vapour to liquid ammonia; namely, $\rho = 5,000$ calories.

Magnus and his collaborators² find for heat of sorption on silica gel about 2,500 calories for argon at 0°, 3,000 for nitrogen, 3,200 for oxygen, 5,600 for ozone, 7,100 for chlorine (at 10°), 7,200 for carbon dioxide, 7,500 for ethylene, and 12,000 for ammonia, the values being somewhat higher for thoroughly evacuated gels, for the initial sorptions, and for lower temperatures. For ammonia the heat is increased if the gel contains an optimum amount of water. Heat of sorption of carbon dioxide by charcoal is nearly the same as with silica gel,³ in both cases being several times the latent heat of condensation of carbon dioxide to liquid carbon dioxide. However, more heat is evolved in the sorption of vapours of organic substances by charcoal than by silica gel.⁴

¹ P. Chappuis, *Wied. Ann. der Physik*, 1883, **19**, 29; also measurements of ammonia and methyl chloride on meerschaum and of air and methyl chloride on charcoal.

² W. Kälberer and H. Mark, *Z. physik. Chem.*, Abt. A, 1928, **139**, 151; W. Kälberer and C. Schuster, *Z. physik. Chem.*, Abt. A, 1929, **141**, 270; A. Magnus, *Z. physik. Chem.*, Abt. A, 1929, **142**, 401; A. Magnus and H. Giebenhain, *Z. physik. Chem.*, Abt. A, 1929, **143**, 265; A. Magnus and K. Grähling, *Z. physik. Chem.*, Abt. A, 1929, **145**, 27; A. Magnus and R. Kieffer, *Z. anorg. allgem. Chem.*, 1929, **179**, 215.

³ A. Magnus and M. Braner, *Z. anorg. allgem. Chem.*, 1926, **151**, 140; A. Magnus, E. Sauter and H. Kratz, *Z. anorg. allgem. Chem.*, 1928, **174**, 142; A. Magnus and H. Kratz, *Z. anorg. allgem. Chem.*, 1929, **184**, 241 (carbon dioxide and ammonia by charcoal and graphite).

⁴ A. P. Okatov, *Zhur. Prikladnoi Khim.*, 1929, **2**, 21.

The additional heat of sorption with bromine and chlorine is quite probably due to chemical reaction with the hydrogen in the charcoal. When 11 g. of charcoal are wetted with 97 g. of bromine, there is a temperature rise of 30° C.¹

Dewar² obtained the values given in table 52 for the heat of sorption by charcoal at — 185° C.

TABLE 52

Heats of Sorption, q , of Gases by Charcoal and their Latent Heats of Vaporization, ρ .

Gas	q Cal.	ρ Cal.
Helium	3,000	24
Hydrogen	1,600	238
Nitrogen	3,684	1,372
Oxygen	3,744	1,664
Argon	3,636	1,500
Carbon monoxide	3,416	1,400
Electrolytic gas	2,414	---
Carbon monoxide and oxygen	3,960	—
Carbon dioxide at — 78°	6,100	3,000

It is noteworthy that in all these cases the heat of sorption q greatly exceeds ρ , the heat of condensation to liquid.³ Again, it is highly significant that there is no essential difference between the values for oxygen, nitrogen and argon. This is in accordance with the general behaviour of the sorption of oxygen at very low temperatures. The three gases are sorbed to much the same extent and their sorption is equally reversible. This is in complete contrast to the be-

¹ Melsens, *Ann. chim. phys.*, (5), 1874, **3**, 522. H. Burstin and J. Winkler (*Przemysl Chem.*, 1929, **13**, 114) propose a method for determining the activity for charcoal from the rise of temperature when it is wetted with benzene.

² J. Dewar, *Proc. Roy. Soc. (London)*, A, 1904, **74**, 122; *Compt. rend.*, 1904, **139**, 261; *Proc. Roy. Inst. Gr. Britain*, 1905, **18**, 182; *Ann. chim. phys.*, (8), 1904, **3**, 5.

³ In many cases, however, the heat of sorption approaches the heat of condensation to liquid; for example, water by building materials (J. W. McBain and J. Ferguson, *J. Phys. Chem.*, 1927, **31**, 564) or by lignite (I. Lavine and A. W. Gauger, *Ind. Eng. Chem.*, 1930, **22**, 1230, where $q = 609.1$ as compared with $\rho = 580.9$ calories per gram of water).

haviour of oxygen at higher temperatures (see this chapter, page 419).

The following results were obtained by Favre ¹ with charcoal :

	NH ₃	CO ₂	N ₂ O	SO ₂	HCl	HBr	HI
<i>q</i>	7,200	7,300	7,400	10,450	9,700	15,500	22,000
<i>p</i>	5,000	6,250	4,400	5,600	3,600	4,000	4,400

The results of Titoff ² for charcoal, using an ice calorimeter, like those of Chappuis, show that heat of sorption is greater in the earlier stages, falling off as sorption proceeds further. Thus for ammonia *q* falls from 11,000 to 7,000 calories, for nitrogen from 8,000 to 4,000 calories, and for carbon dioxide from 7,000 to 6,000 calories. He obtained fair agreement between calorimetric measurements and heats calculated from isosteres.

Lamb and Coolidge ³ have presented the most careful study of the heat of sorption, using steam activated coconut charcoal at 0° with the vapours of eleven organic liquids. Their results are collected in table 53 in which the last column is the molar heat of sorption in the middle of their range where 1 mol of gas is sorbed by 500 g. of charcoal. They found that they

¹ P. A. Favre, *Ann. chim. phys.*, (5), 1874, **1**, 209 (many tables summarizing his results, with references to previous work on various charcoals and on hydrogen by platinum); *Compt. rend.*, 1854, **39**, 729; 1869, **68**, 1300, 1306, 1520; P. A. Favre and J. T. Silbermann, *Compt. rend.*, 1849, **29**, 449; *Ann. chim. phys.*, (3), 1852, **34**, 357; 1852, **36**, 5.

² A. Titoff, *Z. physik. Chem.*, 1910, **74**, 641.

³ A. B. Lamb and A. S. Coolidge, *J. Am. Chem. Soc.*, 1920, **42**, 1146. The following very similar values were obtained with charcoal at 25° C. by J. N. Pearce and L. McKinley (*J. Phys. Chem.*, 1928, **32**, 360): C₂H₅Cl, 11.5 Cal.; CS₂, 12.5; CH₃OH, 13.9; (CH₃)₂CO, 14.4; CHCl₃, 14.5; C₃H₇Cl, 15.4; CCl₄, 15.4; C₆H₆, 15.7; and (C₂H₅)₂O, 15.8 Cal. J. N. Pearce and G. H. Reed (*J. Phys. Chem.*, 1931, **35**, 913) obtain the following additional data: At 25° C., CCl₄, 15.6, CHCl₃, 14.3, CH₂Cl₂, 12.8, CH₃Cl 9.2; and at 50° C., CCl₄, 15.4, CHCl₃, 14.5, CH₂Cl₂, 12.1, CH₃Cl 9.2 Cal., showing a small temperature coefficient, if any. H. K. Cameron (*Trans. Farad. Soc.*, 1930, **26**, 247) showed that for initial sorption (10⁻⁵ mols per gram) the heat of sorption of alcohols by charcoal is very slightly higher than those obtained for more appreciable sorptions, being about 16 and 18 Calories for normal propyl and iso-amyl alcohols, respectively.

could express the heat for changing amounts of sorption by an expression of the form, $q = ax^b$, where a and b are empirical constants, and where x was expressed in total volume of vapour in cubic centimetres at normal temperature and pressure sorbed by 1 gm. of charcoal. q is thus the total or integral heat.

TABLE 53
Heats of Sorption of Vapours by Active Charcoal

Vapour	a	b	q	ρ
C_2H_5Cl . . .	0.7385	0.915	12,000	6,220
CS_2 . . .	0.7525	0.9205	12,500	6,830
CH_3OH . . .	0.742	0.938	13,100	9,330
C_2H_5Br . . .	0.900	0.900	13,900	6,850
C_2H_5I . . .	0.737	0.956	14,000	7,810
$CHCl_3$. . .	0.8285	0.935	14,500	8,000
$HCOOC_2H_5$. . .	0.944	0.9075	14,500	8,380
C_6H_6 . . .	0.774	0.959	14,700	7,810
C_2H_5OH . . .	0.871	0.928	15,000	10,650
CCl_4 . . .	0.803	0.930	15,300	8,000
$(C_2H_5)_2O$. . .	0.917	0.9215	15,500	6,900

The heats of sorption for these various vapours are surprisingly similar.¹ Comparing active with less active charcoal, the values of a and b are found to be much the same.

Another significant fact is that, since the values for b are so nearly equal to unity, the heat of sorption decreases but little with increasing amounts of sorption.² This is in contrast to the data of Titoff and Chappuis previously quoted, but it is in accordance with the regularity observed by Lamb and Coolidge in their own results that the higher the boiling point of the liquid the less does the heat of sorption vary with the amount sorbed. It may be recalled that the higher the boiling point of a liquid the greater, in general, is the latent heat of vaporization (Trouton's rule). The excess of the heat of sorption over the latent heat of vaporization

¹ A. J. Allmand and R. Chaplin (*Proc. Roy. Soc. (London)*, A, 1930, **129**, 256) obtained similar values from isosteres for carbon tetrachloride.

² S. J. Gregg (*J. Chem. Soc.*, **1927**, 1494) finds similar coefficients, using nitrous oxide, acetylene, ethane, carbon monoxide, sulphur dioxide, carbon dioxide, ethylene and nitrogen with activated charcoal.

divided by the molecular volume of the corresponding free liquid at 0° they call the net heat of sorption per cubic centimetre of liquid sorbed. They find that it is nearly identical not only for all their eleven liquids but also for the carbon dioxide and ammonia studied by Titoff. They write: "This is a very illuminating fact. It indicates that the heat of adsorption is indeed due to the attractive forces of the charcoal upon the liquid, and that for a given volume of liquid, that is, for a given volume of filled capillary space, the heat liberated is identical or nearly so for all the liquids studied."

COMPARISON WITH HEATS OF COMPRESSION AND WITH HEATS OF REACTION

Lamb and Coolidge, therefore, proceed to explain the excess of the heat of sorption over the latent heat of vaporization by ascribing it to heat of compression, adopting the classical hypothesis of the thick compressed film. They compute the pressures which must be involved in order to produce the net heats observed, ingeniously taking into account the change in compressibility and in heats of compression at high pressures, and reach the conclusion that 37,000 atmospheres would be required to account for the phenomena. The parallelism between net heats and heats of compression left them with but little doubt that they were the same thing.

This numerical success would be misleading in its consequences if allowed to stand in isolation. A wider perspective is restored if we compare heats of sorption with typical heats of reactions in which there is undoubtedly direct interaction between the molecules of the reactants. Some of these are adduced for comparison in table 54 for the formation of the same hydrates or hydroxides that were quoted in Chapter IV, the data being taken from the tables of Landolt-Börnstein. In table 54 ρ is the latent heat of vaporization of water in calories per mol at the temperature for which the corresponding values for q were obtained, q is the heat of reaction per mol of vapour water in calories, and $q - \rho$ is the heat of reaction per mol of liquid in calories.

TABLE 54

Comparison of Heats of Sorption with Typical Heats of Reactions

Salt	Hydrate	ρ cal./mol	q cal./mol	$q - \rho$ cal./mol
CuSO ₄ . .	CuSO ₄ ·5H ₂ O	10,440	14,150	3,710
BaCl ₂ . .	BaCl ₂ ·2H ₂ O	10,500	14,015	3,515
BaBr ₂ . .	BaBr ₂ ·2H ₂ O	10,500	15,055	4,555
CdSO ₄ . .	3CdSO ₄ ·8H ₂ O	10,500	13,530	3,030
CaSO ₄ . .	CaSO ₄ ·2H ₂ O	10,540	12,876·5	2,336·5
Na ₂ CO ₃ . .	Na ₂ CO ₃ ·10H ₂ O	10,540	12,715·5	2,175·5
MnSO ₄ . .	MnSO ₄ ·4H ₂ O	10,540	13,415	2,875
FeCl ₂ . .	FeCl ₂ ·4H ₂ O	10,540	14,333·75	3,793·75
CaO . .	Ca(OH) ₂	10,540	25,860	15,320
SO ₃ . .	H ₂ SO ₄	10,590	30,990	20,400
H ₂ SO ₄ . .	H ₂ SO ₄ ·H ₂ O	10,740	19,540	8,800
C ₄ H ₆ O ₃ . .	2C ₂ H ₄ O ₂	10,540	23,640	13,100

The data in table 54 resemble corresponding values for sorption so strikingly that it is evident that all the relations involved refer to generalizations which are wider than the scope of any purely chemical or purely physical conceptions. Stress cannot be laid upon a particular success in explaining data according to one special hypothesis without consideration of the whole general subject of chemical and physical interaction. For example, the findings of Lamb and Coolidge are equally explicable in terms of the molecule to molecule hypothesis of Langmuir.

Lamb and Coolidge estimate that the thick compressed film is about forty molecules deep but unfortunately base their calculation on the area estimated by Hulett on the hypothesis of capillary condensation; that is, of liquid under tension.

RELATIONS TO THE CHEMICALS INVOLVED

Gurwitsch¹ found that in the sorption of different liquids by the same amounts of floridin, aluminium trioxide and bone charcoal the greatest heat effects are produced in the sorption of especially reactive substances. He studied water, carbon disulphide and numerous organic compounds belonging to

¹ L. G. Gurwitsch, *J. Russ. Phys.-Chem. Soc.*, 1915, **47**, 805; for similar relations for heat of wetting of potter's clay, silica and sugar, see H. Gaudechon, *Compt. rend.*, 1913, **157**, 209.

different series. Amongst hydrocarbons there is a general increase in heat of sorption as one passes from the naphthene and methane series to aromatic compounds and from these to compounds with double unions, such as those of oxygen and nitrogen, capable of rising to higher valencies. For example, the ratio of heat evolved in the sorption of benzene and toluene by the same amount of different sorbents is for each sorbent nearly the same. The heat effect is greater for chloroform than for carbon tetrachloride, for acetone than for ethyl acetate, for methyl alcohol than for ethyl alcohol, and for the latter than for amyl alcohol. In each group of compounds the heat of sorption may serve as an approximate measure of reactivity, as exemplified by velocities of esterification or heats of formation of organic magnesium compounds.

The heat of sorption of alcohol on thoria is estimated by Hoover and Rideal¹ to be 14,000 calories at first, falling with further sorption to 9,900 calories which they interpret as heat of condensation. Heats of sorption and of wetting for zinc oxide have been measured by Ewing,² using benzene, xylene, pyridine and water; further, he has measured heat of sorption of carbon dioxide, sulphur dioxide and ammonia. There is no connexion between heat of sorption and retentivity, water and carbon dioxide being readily removed, pyridine and sulphur dioxide not. Heat of sorption of hydrogen by zinc-chromium oxide depends upon the amount of chemical reduction and upon the previous treatment with hydrogen, values obtained ranging between 6,000 and 20,000 calories.³

Goldmann and Polányi,⁴ using charcoal, express the sorption x of the four vapours they studied in the form of differential free energy A_x and differential heat of sorption $\bar{q}_x$. $A_x = RT \ln p_s/p_x$ where p_s is the vapour tension or saturation pressure of the liquid and p_x is the equilibrium pressure

¹ G. I. Hoover and E. K. Rideal, *J. Am. Chem. Soc.*, 1927, **49**, 122.

² W. W. Ewing, *Ind. Eng. Chem.*, 1931, **23**, 427.

³ E. W. Flosdorf and G. B. Kistiakowsky *J. Phys. Chem.*, 1930, **34**, 1909.

⁴ F. Goldmann and M. Polányi, *Z. physik. Chem.*, 1928, **132**, 321.

for sorption equal to x . They deduce the heat of sorption from the general thermodynamic equation, $q_x = A_x - T \left(\frac{\partial A_x}{\partial T} \right)_x$. The remarkable forms of the graphs of q_x against x are shown in figs. 125, 126, 127 and 128.¹ On the other hand, Ganguli² and others would take heat of sorption to be practically equal to adsorption potential A ; Ganguli points out that it

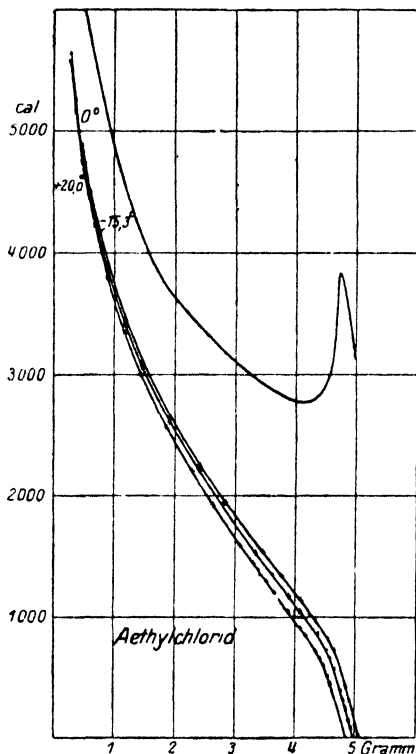


Fig. 125.—Goldmann and Polányi Graphs of Free Energy Curves of Sorption ($RT \ln p_s/p$) in Calories for various Amounts of Sorption (in grams) of Ethyl Chloride on Charcoal at three Temperatures and the Graph for Heat of Sorption derived therefrom.

¹ F. Goldmann and M. Polányi, *Z. physik. Chem.*, 1928, **132**, 336 and 337, figs. 3, 4, 5 and 6.

² A. Ganguli, *J. Phys. Chem.*, 1930, **34**, 665.

may likewise be equal to heat of sublimation of the pure solid. These approximations cannot be exact or quite general. For example, the heat of sorption of benzene on charcoal exceeds the heat of sublimation by 26 per cent.

Patrick and Greider,¹ using water and silica gel, find that

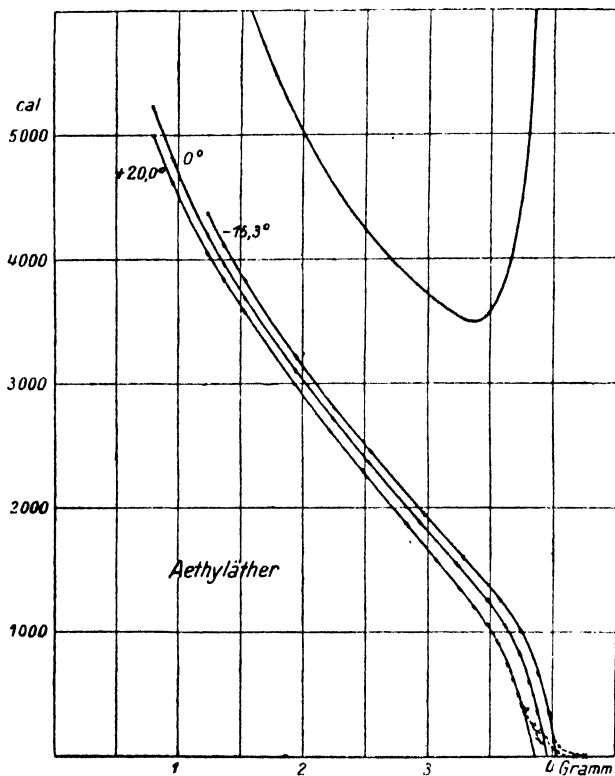


Fig. 126.—Goldmann and Polányi Graphs of Free Energy Curves of Sorption ($RT \ln p_s/p$) in Calories for various Amounts of Sorption (in grams) of Ethyl Ether on Charcoal at three Temperatures and the Graph for Heat of Sorption derived therefrom.

¹ W. A. Patrick and C. E. Greider, *J. Phys. Chem.*, 1925, **29**, 1031. E. Bosshard and E. Jaag (*Helv. Chim. Acta*, 1929, **12**, 105) found that various silica gels when thrown into water yield between 16 and 32 calories per gram of gel.

the heat of sorption, as measured in an ice calorimeter, follows the Lamb-Coolidge equation, a being 1.091 and b 0.914. At saturation 1 gm. of gel takes up 0.3612 g. of water. They

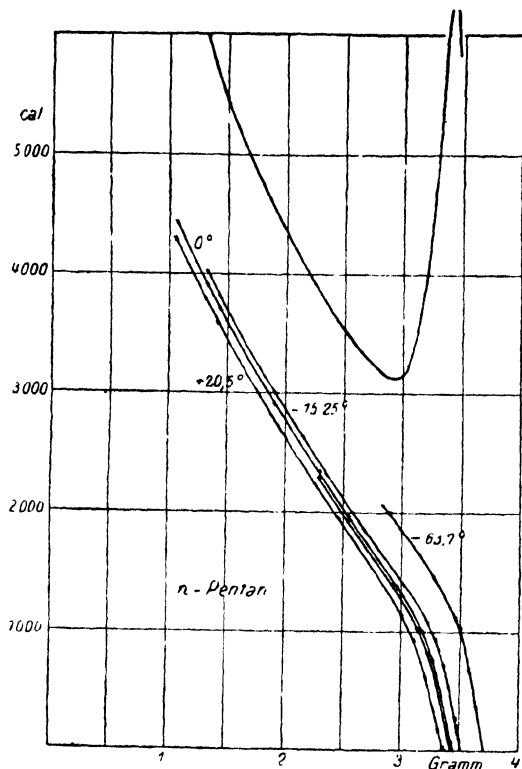


Fig. 127.—Goldmann and Polányi Graphs of Free Energy Curves of Sorption ($RT \ln p_s/p$) in Calories for various Amounts of Sorption (in grams) of *n*-pentane on Charcoal at five Temperatures and the Graph for Heat of Sorption derived therefrom.

confirm that the difference between the heat evolved by that amount of water, 236.2 calories, and its heat of liquefaction at 0° C., 215.6 calories; namely, 20.6 calories, is equal to the experimentally determined heat of melting, 19.22 calories at 25° C. For sulphur dioxide a is 0.316 and b is 0.860, the

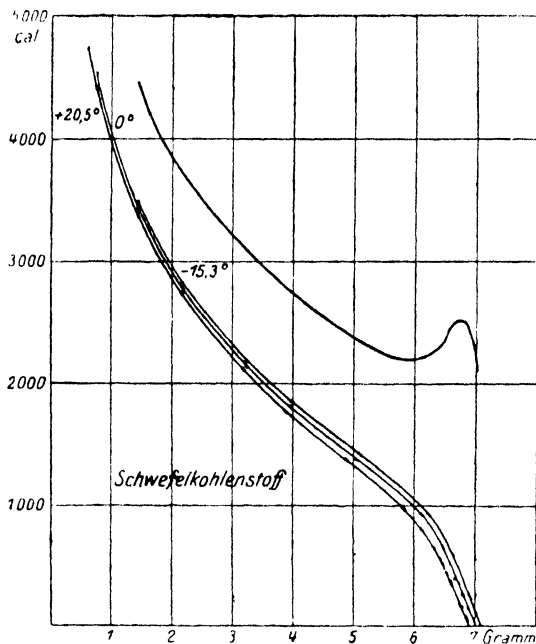


Fig. 128.—Goldmann and Polányi Graphs of Free Energy Curves of Sorption ($RT \ln p_s/p$) in Calories for various Amounts of Sorption (in grams) of Carbon Disulphide on Charcoal at three Temperatures and the Graph for Heat of Sorption derived therefrom.

net heat at saturation being practically the same as that for water.

HEATS FOR WATER AND MERCURY

Coolidge¹ has discovered the only two cases where heat of sorption is less than the heat of condensation. For the sorption of water by purified activated coconut charcoal and by especially pure steam activated sugar charcoal, the isotherms are identical at temperatures between 20° and -30° C. Hence the heat of sorption² is exactly equal to ρ . At higher

¹ A. S. Coolidge, *J. Am. Chem. Soc.*, 1927, **49**, 708, 1949.

² But see the much higher values obtained by T. Okazawa, *Bull. Inst. Phys. Chem. Research* (Tokyo), 1928, **7**, 821; English Ed., **1**, 75. All observed heats of wetting of charcoal by water are positive

temperatures more water is sorbed ; hence the heat of sorption is less than ρ . Moreover, the heat of sorption increases with increasing sorption, contrary to all previous cases studied, except perhaps the calorimetric data of Williams¹ which showed a minimum in heat of sorption of sulphur dioxide on "blood charcoal". From this one may conclude that the heat capacity of the system, charcoal + sorbed water, exceeds that of the separate components.

Even more remarkable is the behaviour of mercury with activated coconut charcoal.² From the isostere for 1 milligram of mercury per gram of charcoal, the heat of sorption deduced is 8,900 calories which is much less than the heat of evaporation, 13,000 calories. Hence, although the heat of sorption of mercury vapour is very strongly exothermic, the heat of sorption (or melting) of liquid mercury is markedly endothermic. Therefore, at room temperature charcoal will largely free itself from mercury if the partial pressure of the mercury is great enough to form liquid mercury. Thus Coolidge's charcoal sorbed a minimum of 0.3 mg. of mercury at 20° C. and 69 mg. at 360° C. per gram of charcoal. It is probable that mercury vapour can displace appreciable amounts of permanent gases from charcoal.

ERRORS IN INITIAL HEATS OF SORPTION

Care has to be taken that the heats of sorption observed are not vitiated by disturbances due to unsuspected impurities in the sorbing material. Thus Coolidge³ found it necessary to extract coconut charcoal with hydrofluoric acid for several days and afterwards to steam it out for a month to reduce the ash from 1.7 to 0.4 per cent and thus to eliminate the irreversible sorption of small amounts of sulphur dioxide.

instead of being zero or negative as would be deduced from the data of Coolidge and also those of F. G. Keyes and M. J. Marshall (*J. Am. Chem. Soc.*, 1927, **49**, 163) ; see Chapter IV, page 147, footnote 1.

¹ A. M. Williams, *Proc. Roy. Soc. Edin.*, 1917, **37**, 161 ; see also M. Polányi and K. Welke, *Z. physik. Chem.*, 1928, **132**, 371.

² A. S. Coolidge, *J. Am. Chem. Soc.*, 1927, **49**, 708, 1949.

³ A. S. Coolidge, *J. Am. Chem. Soc.*, 1927, **49**, 708.

Such a source of error becomes greatly magnified when studying initial sorptions of small amounts. A case in point is that of Magnus and Kälberer ¹ who found a heat of sorption for carbon dioxide by animal charcoal, which had previously been heated to 100°, of only 846.7 calories for a pressure of 0.9 mm.; whereas, if the charcoal had been previously heated to 600°, the heat of sorption was 12,462 calories for a pressure of 0.076 mm. This was subsequently traced to the calcination of the calcium carbonate present as an impurity. Their value for the sorption of carbon dioxide by silica gel was 7,174 calories for a pressure of 6.3 mm., falling almost linearly to 6,098 calories at a pressure of 538.4 mm. The heat of sorption of carbon dioxide on charcoal calculated from isosteres by Dixon ² differs by several thousand calories from those measured by Magnus and Kälberer, this difference being of the approximate magnitude of the heat of vaporization of liquid carbon dioxide. The data of McLean ³ indicate that the heat of sorption of carbon dioxide by various lignites and coconut charcoal exceeds the latent heat of vaporization by at least five-fold and sometimes much more.

Serious error is occasioned by low thermal conductivity at low pressures.

Garner and McKie ⁴ on adding extremely small amounts of oxygen to charcoal found that the initial heat was almost zero. Later, however, Bull and Garner ⁵ showed that this was partly due to porous sorbents being excessively bad conductors of heat in vacuo. They show that this factor has been insufficiently taken into account in all previous work. Some doubt is, therefore, cast upon the values obtained by Kistiakowsky, Flosdorf and Taylor ⁶ and by Fryling ⁷ for the

¹ A. Magnus and W. Kälberer, *Z. anorg. allgem. Chem.*, 1927, **164**, 357; A. Magnus, *Z. Elektrochem.*, 1928, **34**, 531.

² J. K. Dixon, *J. Phys. Chem.*, 1930, **34**, 870.

³ S. McLean, *Trans. Roy. Soc. Canada*, (3), 1921, **15**, 74.

⁴ W. E. Garner and D. McKie, *J. Chem. Soc.*, 1927, 2451.

⁵ H. I. Bull and W. E. Garner, *Nature*, 1929, **124**, 409.

⁶ G. B. Kistiakowsky, E. W. Flosdorf and H. S. Taylor, *J. Am. Chem. Soc.*, 1927, **49**, 220.

⁷ C. F. Fryling, *J. Phys. Chem.*, 1926, **30**, 818.

low initial heats of sorption of hydrogen on copper and on nickel, respectively. It had been suggested that the initial heat of sorption of hydrogen on copper might have been compensated by an activation of particular portions of the sorbent and by a dissociation of the hydrogen into atoms in the most active points of the sorbent; an interpretation that is thermodynamically unsound.^{1, 2}

Marshall and Bramston-Cook³ have measured in an ice calorimeter the differential heat of sorption of oxygen by coconut charcoal where x was in one case as low as 0.136×10^{-5} mols per gram of charcoal or 0.03 c.c. per gram of charcoal,

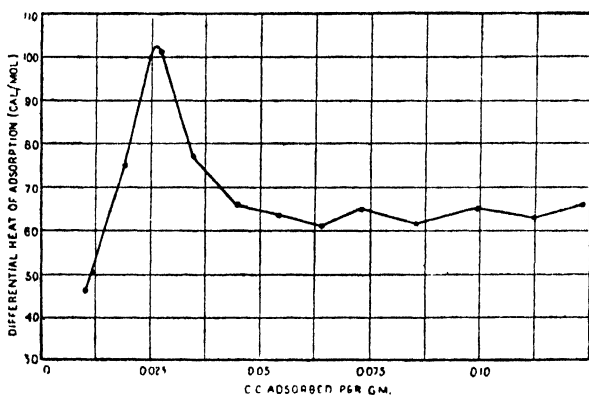


Fig. 129.—Differential Heat of Sorption of Oxygen on Charcoal at 20° C. and extremely low Pressures (Bull and Garner).

indicating a heat of sorption for zero concentration of 89,600 calories. Bull and Garner⁴ used still smaller additions of oxygen at a time and obtained the curve shown in fig. 129 and a similar curve for nitric oxide on charcoal. They conclude: "It is difficult to decide whether the above phenomena

¹ M. Polányi and K. Welke, *Z. physik. Chem.*, 1928, **132**, 371.

² K. F. Herzfeld, *J. Am. Chem. Soc.*, 1929, **51**, 2608.

³ M. J. Marshall and H. E. Bramston-Cook, *J. Am. Chem. Soc.*, 1929, **51**, 2019.

⁴ H. I. Bull and W. E. Garner, *Nature*, 1929, **124**, 409, fig. 1. See also the additional confirmatory measurements of H. K. Cameron, *Trans. Farad. Soc.*, 1930, **26**, 239.

are due to activation of the carbon surface or to incompleteness of the reaction between oxygen and carbon at low surface concentrations. The experimental evidence is, however, in favour of the latter hypothesis."

SORPTION OF OXYGEN BY CHARCOAL

The results obtained in the measurement of the heat of sorption of oxygen by charcoal are of especial interest. The value obtained by Dewar at the temperature of liquid air, 3,744 calories, has already been commented upon. Keyes and Marshall¹ found, at 0° C., 72,000 calories for the differential heat of sorption on activated charcoal for the initial amounts of oxygen sorbed. This heat dropped slowly as x increased to about 1.5×10^{-5} mols per gram of charcoal; as x increased beyond this value, the heat of sorption fell off rapidly to a constant value of 4,300 calories.

Garner and his collaborators² find that the heat of sorption of oxygen by charcoal ("Norit") for $x = 1 \times 10^{-5}$ mols per gram of charcoal rises from 70,000 calories at 18° C. to 115,000 or 116,000 at 200° C. and to the astonishing value of 224,000 calories at 450° C. Their results are illustrated in fig. 130³ where Q is the heat of sorption in kilogram calories.

"Up to 100° C. only negligible amounts of carbon dioxide are produced on admitting oxygen to the charcoal, but at higher temperatures this gas is liberated in increasing amounts. At 450° more than 30 per cent of the oxygen combining with the surface is liberated as dioxide. This makes the deduction of the heat of adsorption uncertain. Nevertheless, we believe the general trend of the curve to be correct."

¹ F. G. Keyes and M. J. Marshall, *J. Am. Chem. Soc.*, 1927, **49**, 156; see also A. F. H. Ward and E. K. Rideal, *J. Chem. Soc.*, 1927, 3117; A. G. R. Whitehouse, *J. Soc. Chem. Ind.*, 1926, **45**, 13T. Keyes and Marshall also made measurements with water, chlorine, ammonia, carbon dioxide, ethyl ether and chloropicrin.

² E. A. Blench and W. E. Garner, *J. Chem. Soc.*, 1924, **125**, 1288; W. E. Garner and D. McKie, *J. Chem. Soc.*, 1927, 2451; D. McKie, *J. Chem. Soc.*, 1928, 2870; W. E. Garner, *Nature*, 1924, **114**, 932.

³ W. E. Garner and D. McKie, *J. Chem. Soc.*, 1927, 2455, fig. 2.

The heat of sorption just above 100° is approximately equal to the heat of combustion of the oxygen to carbon dioxide plus the heat of sorption of that carbon dioxide. The often quoted value at 450° is over twice as great. It very much needs confirmation in view of its fundamental significance if substantiated. It would be accounted for if the heat were due to the oxygen combining with some of the hydrogen present in the charcoal. The charcoal had been

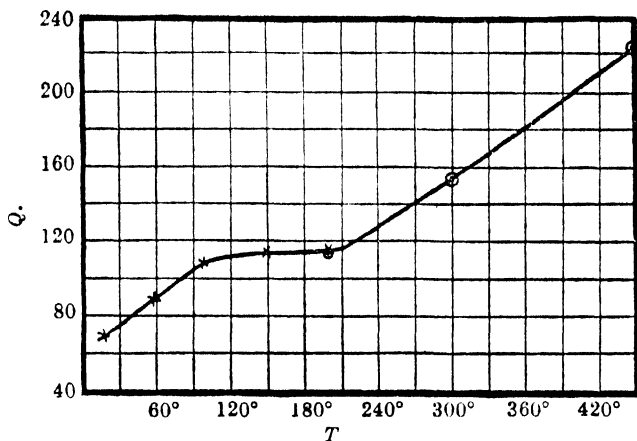


Fig. 130.—Heat of Sorption Q of Oxygen on Charcoal at various Temperatures (Garner and McKie).

heated to only 900° and at this temperature charcoals almost invariably still contain 0.5 per cent by weight of hydrogen; that is, about one atom of hydrogen for every seventeen atoms of carbon. This source of error was not especially provided for during the course of the investigation, but the authors state: "the heat of adsorption under given conditions is not appreciably affected by repeated treatment of the carbon surface with oxygen. It is thus unlikely that any of the heat liberated was due to the heat of combustion of gases adsorbed on the surface of charcoal." The authors suggest that at very low temperatures the molecule of oxygen is held by a carbon atom without electron transference or sharing. At

moderate temperatures one of the valencies of the oxygen molecule may be broken for attachment to a carbon atom ; such a complex should desorb as carbon dioxide. At still higher temperatures the oxygen may be sorbed as atoms held by separate carbon atoms and this would desorb as carbon monoxide.

HEATS OF SORPTION ON METALS ¹

Gillespie and Hall ² calculated the heat of sorption of hydrogen by palladium which amounted to about 6,000 calories at low hydrogen content and about 8,860 calories along the horizontal isotherms, rising to about 9,740 calories for further additions. For the arbitrary composition $2(\text{Pd}_2\text{H})$ they calculate 8,780, 8,700 and 8,450 calories at 0°, 30° and 80° C., respectively. These results agree with that of Mond, Ramsay and Shields.³

Foresti ⁴ found for the heat of sorption of hydrogen on nickel 20,000 falling to 15,000 calories. Beebe and Taylor ⁵ obtained 20,000 calories which they compare with the estimated heat of condensation of hydrogen, $p = 650$ calories (fictitious, of course, at high temperatures). They conclude that sorption of hydrogen by nickel is far more drastic in its nature than mere physical condensation. Johnson ⁶ found that the heat of sorption of atomic hydrogen on glass was 11,000 calories.

¹ W. G. Palmer attempted on a rather uncertain basis to calculate heats of sorption from coherer voltages for tungsten, platinum and carbon in the presence of various gases ; the results ranged from negligible to very large values and depended upon the previous treatment of the metal (*Proc. Roy. Soc. (London)*, A, 1924, **106**, 67 ; 1926, **110**, 141).

² L. J. Gillespie and F. P. Hall, *J. Am. Chem. Soc.*, 1926, **48**, 1218.

³ See this chapter, page 424, footnote 2.

⁴ B. Foresti, *Gazz. chim. ital.*, 1923, **53**, 487 ; 1924, **54**, 132 ; 1925, **55**, 185. Also measurements of ethylene (5845.6 calories) and ethane (5004.7 calories) on nickel.

⁵ R. A. Beebe and H. S. Taylor, *J. Am. Chem. Soc.*, 1924, **46**, 43. Also measurements of hydrogen on copper.

⁶ M. C. Johnson, *Proc. Roy. Soc. (London)*, A, 1929, **123**, 612.

For ammonia, Dew and Taylor¹ find heats of sorption at very low partial pressures of 16,000 calories for iron, 11,300 for nickel and 8,700 for copper, the values falling considerably at higher pressures.

A summary of the results obtained by Taylor and his collaborators with metals and their interpretation with particular reference to contact catalysis has recently been made by Taylor. They^{2,3} consider the unresolved difficulties in the way of accepting, without ample evidence, apparent maxima in heats of sorption. Further, it is pointed out that although hydrogen may be assumed to dissociate into atoms, this could hardly account for the corresponding minimum and maximum values obtained by Kistiakowsky for carbon monoxide on copper.⁴

In the course of his discussion Taylor presents the following further data by Kistiakowsky for sorption of gases by platinum black, such as 30,000 calories for hydrogen, sulphur dioxide and carbon monoxide; whilst a very active preparation made by the reduction of platinum chloride with formaldehyde gives a heat of sorption for oxygen at 0° of $q = 104,000$ calories, falling from an initial value of $q = 161,000$ calories. The initial value, however, may have been due to reaction with the hydrogen on the platinum black.

Taylor's results indicate that there is no relation between heat of sorption and the firmness by which sorbed molecules are held. Thus water vapour with a heat of sorption on platinum of 55,000 calories is readily pumped off, in contrast to the behaviour of carbon dioxide and sulphur dioxide with heats of sorption which are less than 35,000. Additional data obtained by Washburn are adduced for the heats of sorption of hydrogen, ethylene and ethane by copper at 0°; namely, 11,300, 16,000 and 11,000, respectively. Here the

¹ W. A. Dew and H. S. Taylor, *J. Phys. Chem.*, 1927, **31**, 285 (integral and differential heats).

² K. F. Herzfeld, *J. Am. Chem. Soc.*, 1929, **51**, 2608.

³ H. S. Taylor, *Z. Elektrochem.*, 1929, **35**, 542.

⁴ H. S. Taylor and G. B. Kistiakowsky, *Z. physik. Chem.*, 1927, **125**, 341; G. B. Kistiakowsky, *Proc. Nat. Acad. Sci.*, 1927, **13**, 3.

hydrogen is strongly sorbed, and ethane, with the same heat of sorption, is only weakly sorbed. Rideal found 40,000 and 12,000 for hydrogen on active and inactive copper catalysts, respectively.

It is interesting that H. S. Taylor and Kistiakowsky¹ found that a slight oxidation of a copper surface changed a low initial heat of sorption of hydrogen into a very high one. Other experiments of G. B. Taylor, Kistiakowsky and Perry² relate to hydrogen, oxygen, sulphur dioxide and carbon monoxide on platinum black. In some cases the sorption was carried out on black already contaminated by one of the other gases. The sorption and the heat of sorption for oxygen and for hydrogen placed various blacks in the order of their catalytic activity. Further work upon the sorption of hydrogen, oxygen and water vapour alone and successively on platinum black was carried out by Flosdorf and Kistiakowsky.³ The heats of sorption for hydrogen lay between 21,000 and 55,000 calories, those for oxygen between 60,000 and 83,000, and those for water between 16,000 and 35,000.

COMPILATION OF HEATS OF SORPTION AND HEATS OF WETTING⁴

Up to 1927 a compilation of the more accurate data for heats of sorption has been made by Kruyt and Modderman.⁵

¹ H. S. Taylor and G. B. Kistiakowsky, *Z. physik. Chem.*, 1927, **125**, 341; G. B. Kistiakowsky, *Proc. Nat. Acad. Sci.*, 1927, **13**, 3. E. B. Maxted (*J. Chem. Soc.*, 1930, 2093) did not remove oxygen from platinum black before measuring initial heats with hydrogen.

² G. B. Taylor, G. B. Kistiakowsky and J. H. Perry, *J. Phys. Chem.*, 1930, **34**, 799.

³ E. W. Flosdorf and G. B. Kistiakowsky, *J. Phys. Chem.*, 1930, **34**, 1911.

⁴ C. M. Pouillet, *Ann. chim. phys.*, (2), 1822, **20**, 141.

⁵ H. R. Kruyt and J. G. Modderman, *International Critical Tables*, 1929, **5**, 139. For older references see G. J. Parks, *Phil. Mag.*, (6), 1902, **4**, 240. The heat of wetting by water above and below 4°C. is of special interest because C. G. Jungk (*Pogg. Ann. der Physik*, 1865, **125**, 292) and later G. Schwalbe (*Ann. der Physik*, (4), 1905, **16**, 32) found it positive below 4° and negative above. S. Lagergren *Bihang t. K. Svenska Vet. Akad. Handl.*, 1899, **24**, Afd. II, No. 5) pointed out that if the sorbed water is under a pressure such as 6,150

Later data are given as a supplement to the brief monographic treatment of the subject, published in 1930.¹ References to all the papers from which they quote data are to be found in previous footnotes.² They also quote data for wetted blood charcoal (Merck) brought into contact with solutions of crystal violet³ and of the nitrates of lithium, potassium and caesium, which prove that there is a distinct, although small, heat of sorption above that of mere heat of wetting.⁴ The same compilation includes the best values for heats of wetting. For organic liquids it is about 30 calories

atmospheres, the heat of compression becomes positive and the temperature of maximum density of water goes below 0°. M. Bellati (*Atti ist. Veneto*, 1900, **59**, 2. Teil, 931; M. Bellati and F. Finazzi, *Atti ist. Veneto*, 1902, **61**, 503) found it negative at 0° C. for a certain small range of added water, above and below which it was positive; see W. A. Patrick, *Colloid Sym. Annual* (Johns Hopkins, 1929), 1930, **7**, 129; W. A. Patrick and F. V. Grimm, *J. Am. Chem. Soc.*, 1921, **43**, 2144. Further experiment is required. See also T. Martini, *Atti ist. Veneto*, 1904, **63**, 915; *Beibl. Ann. der Physik*, 1905, **29**, 69, 71; H. Freundlich, *Kapillarchemie*, 1930, **1**, 238; A. Eucken, *Handbuch der Experimentalphysik*, Wien-Harms, 1929, **8**, Teil 1, "Energie- und Wärmeinhalt," p. 668.

¹ H. R. Kruyt and J. G. Modderman, *Chem. Reviews*, 1930, **7**, 259-346. The writer would take exception to the opening statement that the heat of sorption is the difference in energy of the gas before and after sorption. Neither is it the difference in energy of the carbon, copper or other solid before and after it has sorbed a gas; both are involved.

² With the addition of L. Mond, W. Ramsay and J. Shields' measurements for oxygen and hydrogen on platinum, platinum black and palladium black at 0° with an ice calorimeter, giving 9,362 calories per mol (*Phil. Trans. Roy. Soc. London*, A, 1897, **190**, 129; 1898, **191**, 105; *Z. physik. Chem.*, 1898, **25**, 657). A. Eucken (*Handbuch der Experimentalphysik*, Wien-Harms, 1929, **8**, Teil 1, "Energie- und Wärmeinhalt," pp. 649-668) has discussed the subject of heat of sorption.

³ H. R. Kruyt and Jac. van der Spek, *Kolloid-Z.*, 1919, **24**, 145; H. Lachs and F. Lachman, *Z. physik. Chem.*, 1926, **123**, 303.

⁴ See also P. Reh binder and L. Krajuschkina, *Z. physik. Chem.*, Abt. A, 1929, **142**, 282 (iso-amyl alcohol in aqueous solution and butyric acid in water and in hexane with silica gel and with charcoal); B. Iliin and B. Rosanow, *Z. Physik*, 1929, **55**, 285 (various concentrations of methyl alcohol in water with wood charcoal and glass powders); M. M. Chilikin, *Zhur. Prikladnoi Khimii*, 1930, **3**, 221 (sodium hydroxide with cellulose; also heat of wetting with 50 per cent alcohol).

per gram of active charcoal as compared with, say, 12.35 calories for water.¹ Glass wool exposed to nearly saturated water vapour yields no further heat upon immersion in water, whereas dry glass or silica yields 0.00105 calories per square centimetre.² The heat of wetting of anhydrous silica is about 16.6 for alcohol and acetone.³ Heats of wetting are also collected and discussed by Krczil.⁴ From heats of wetting, heats of sorption of the unsaturated vapour may be deduced as Hedges⁵ has illustrated for water vapour with silk and wool.

¹ K. Andress and E. Berl, *Z. physik. Chem.*, 1926, **122**, 81; E. V. Alekseevski, *Zhur. Prikladnoi Khim.*, 1928, **1**, 182 (19 organic substances and water).

² G. J. Parks, *Phil. Mag.*, (6), 1903, **5**, 517.

³ F. E. Bartell and Y. Fu, *Colloid Sym. Annual* (Johns Hopkins, 1929), 1930, **7**, 135.

⁴ F. Krczil, *Untersuchung und Bewertung technischer Adsorptionsstoffe*, pp. 180-198 (Akademische Verlagsgesellschaft, m.b.H., Leipzig, 1931).

⁵ J. J. Hedges, *Trans. Farad. Soc.*, 1926, **22**, 178.

PART III

HYPOTHESES AND THEORY OF SORPTION

CHAPTER XV

A BRIEF CLASSIFICATION OF SORPTION HYPOTHESES

Hypotheses of sorption and explanations of its mechanism are based chiefly upon the data obtained for the sorption of gases and vapours. These are taken as representing the simplest and therefore theoretically most significant cases. However, it should be remembered that there are manifold phenomena which present themselves only in sorption from solutions and which lie outside the scope of this volume.

Current hypotheses may be listed as follows :

(1) *Capillary Condensation*.—This assumes that vapours are condensed as bulk liquid in pores owing to the lowering of vapour pressure due to the effects of surface tension. It is discussed in detail in Chapter XVI. Such condensation must inevitably take place whenever pores of suitable size are exposed, at pressures approaching saturation, to the vapour of liquids that can wet the surface. However, it is not an explanation of sorption in general, even where it occurs. It cannot explain either sorption upon truly plane surfaces or the sorption of gases. It is therefore an additional supernumerary phenomenon.

(2) *The Classical Hypothesis of a Thick Compressed Film*.—This assumes the existence of long range attractive forces extending out from the surface of a solid. It was fully accepted for a century, but now is retained only by a minority. According to the current theory of atomic structure, no forces

are provided for which operate over a distance of a few Ångstrom units. As to whether such forces do actually exist, the verdict must be the Scottish one of "not proven" rather than "disproven". Observations such as those of Sir William Hardy and Miss Nottage unless vitiated by the intrusion of unsuspected error would constitute a direct proof of their existence and effectiveness (see Chapter X, page 350). The compressed film hypothesis is presented in its various forms in Chapter XVII. Attempts made by Williams in 1919 and Polányi in 1928 to restrict the range of molecular action depicted have become in practice variants of the following hypotheses, (3) and (4).

(3) *Monomolecular Adsorption*.—The essence of the large number of hypotheses of monomolecular and monatomic adsorption, many of which were described or indicated by Langmuir, is that forces operate practically only between molecules or atoms that are in actual contact. These views are presented in Chapter XVIII.

(4) *Multilayer Adsorption*.—This is essentially a variant of the last hypothesis (3). In a few cases a monatomic layer of one substance such as oxygen is adsorbed upon a monatomic layer of another such as thorium which in turn is adsorbed upon tungsten. In most cases, however, it is used to explain the building up of thick films on plane surfaces exposed to nearly saturated vapours.

(5) *Monomolecular Adsorption with Chains of Oriented Molecules extending far into a Liquid*.—This hypothesis is only applicable to liquids and solutions in which the molecules are close packed already. There is a large amount of varied evidence for it, but this again lies outside the present discussion. It may be regarded as an extension of hypotheses (3) and (4).

Hypotheses (1), (2), and (4) are purely physical, (3) embraces physical and chemical adsorption equally, while (5) is essentially physical.

There are actually at least two types of adsorption, physical and chemical. For example, compare the behaviour of oxygen with charcoal at low, medium and high temperatures

(Chapter I, page 9). In practice, a strict attempt to confine the discussion to proven cases of purely physical adsorption on true surfaces would exclude most of the experimental data of sorption with gases and vapours and almost all of the observations made with solutions.

Any physical explanation must needs be of general applicability and will overlie any specific or chemical adsorption, although such specific effects abound. Hence it is of vital importance to decide between hypotheses (2), (3), and (4) for gases. The crucial questions are: Is the sorbed layer of the order of 100 to 10,000 molecules thick or only one (which in special circumstances can be built up into two or more)? Is the range of molecular attraction comparable only to molecular or atomic diameters, or is it of the order of 10,000 Å. as found by the older physicists? Do molecules act upon one another at great relative distances or are such attractive forces confined to molecules in actual contact? The whole trend of modern physics is based upon the last assumption. The experimental evidence is reviewed in Chapter X and is found to be inconclusive and difficult to assign wholly to either hypothesis. Even if the sorbed layer is only about one molecule deep, are the attractive forces so continuous over the surface and so non-localized that the ordinary equation of state may apply without modification to the two-dimensional layer?

It is a remarkable fact that we cannot decide between these hypotheses by mere comparison of the data with the formulæ corresponding to each of the hypotheses listed. It is almost laughable to see how the same data (generally those for carbon dioxide by Titoff, Richardson and Miss Homfray) are adduced as verification. Each hypothesis scores a numerical triumph for the same data.

The difficulty is largely due to the paucity or total lack of absolute measurements with surfaces sufficiently known to be acceptable to critical experimenters, and observations on each surface made under a sufficiently wide range of conditions to display the possible factors. Many of the arguments employed are found on closer analysis to involve general

behaviour common to physical and chemical interactions alike.

The writer believes that it is possible to devise crucial experiments to decide between these hypotheses for particular cases, and he would refer to the experiments of J. L. Porter in his laboratory upon the expansion of charcoal exposed to various vapours, including water, as a disproof of the hypothesis of capillary condensation as sole explanation, and the experiments of his other collaborator Britton upon the effect of high pressures in the sorption of nitrogen by charcoal as a disproof of the applicability of hypothesis (2) for the major portion of the sorbed nitrogen. It is quite probable that experiments with finely porous bodies such as charcoal or silica gel cannot decide, simply because the pores are so fine that there is no room for the display of the characteristic behaviour of hypotheses (1), (2), and (4).

On the whole, theories and observations appear to focus on the Langmuir formulation which has been obtained by many investigators by very many lines of approach. The Langmuir formula gives an isotherm or isotherms but not a temperature coefficient. The Eucken-Polányi formulations give a temperature coefficient but no isotherm. The Williams-Henry formulation gives both. When all are approximately or exactly identified we attain to a much more complete formulation. The Eucken-Polányi and the Langmuir theories have been criticized for not comprising a temperature coefficient for the attractive forces or for the amount of maximum saturation, but the Langmuir conceptions are greatly enriched by the recognition in certain cases of the mobility in sorbed films and the behaviour on heating of gases, vapours and liquids.

A thorough search necessitates reference to a number of related fields in special studies as, for example, crystallography, lubrication, adhesives and others of which only contact catalysis will be briefly included in this volume. If Langmuir is correct, that in general collisions of a molecule of gas or vapour with the solid are inelastic, then the primary process of adsorption is always physical. This may or may not in

particular cases be followed quickly or slowly by other physical or chemical processes, justifying either by their indefiniteness or by actual complexity the comprehensive title of sorption.

CHAPTER XVI

CAPILLARY CONDENSATION

DEPENDENCE OF CONDENSATION IN CAPILLARIES UPON VAPOUR PRESSURE

Since porous bodies sorb *par excellence*, it is an obvious suggestion to attempt to relate sorption to behaviour in capillary tubes. This was done for silicic acid jellies by Zsigmondy¹ in 1911. Zsigmondy showed by means of the ultramicroscope that such jellies consist of ultramicroscopic particles in loose contact or aggregation with many irregular spaces between. He considered that each particle was covered with an adsorbed layer of water molecules but that under suitable conditions of vapour pressure, liquid water could condense in the large irregular spaces. Zsigmondy, therefore, followed the very clear distinction drawn by Wilhelm Ostwald² between adsorbed and capillary condensed liquids, which are independent of each other and due to different causes, although necessarily in equilibrium with the same vapour. Patrick,³ however, who in 1914 expressed Zsigmondy's view, has since appeared as the extreme protagonist for the general hypothesis that all of the sorbed material in a porous body is liquid condensed in its capillaries.

The quantitative relations between capillarity and vapour pressure follow from the treatment of Thomson⁴ and are visualized in the accompanying diagram, fig. 131, which shows a liquid which has risen in an open capillary tube, where it is obvious that the concave meniscus at the top of the capillary

¹ R. Zsigmondy, *Z. anorg. Chem.*, 1911, **71**, 356.

² Wilhelm Ostwald, *Lehrbuch der allgem. Chem.*, Zweite Aufl., 1906, Bd. II, Abt. 3, p. 242.

³ W. A. Patrick, *Dissert.*, Göttingen, 1914.

⁴ W. Thomson, *Phil. Mag.*, (4), 1871, **42**, 448.

tube is in equilibrium with the vapour of appreciably lower pressure than that in equilibrium with the plane surface of the liquid in bulk. The connexion between surface tension and the two vapour pressures is given by the formula,

$$\ln \frac{p}{p_s} = \frac{-2\sigma v}{rRT},$$

where p is the pressure at the concave surface, p_s the pressure of saturated vapour of liquid in bulk at that temperature, σ is the surface tension, v is the volume of one gram mol of condensed liquid, r is the radius of the capillary, R the gas constant (8.315×10^7 ergs), T the absolute temperature, and $\ln$ represents the natural logarithm to the base e . The radius r may be deduced from the formula,

$$r = \frac{2\sigma d_{\text{gas}}}{p_s d_{\text{liquid}}} \cdot \ln \frac{p}{p_s},$$

where d represents density of vapour and liquid, respectively. Zsigmondy does not regard r as half the distance between the walls or particles but rather as half the distance between the adsorbed films. Patrick, on the other hand, does not approve of this calculation of r for very small pores (see later). For liquids with the surface tension of water, if $p/p_s = 0.5$, the largest radius of the pores holding water is $15 \text{ \AA.}$; that is, the vapour must be more than half saturated if it is to condense in any pores larger than $15 \times 10^{-8} \text{ cm.}$ or $15 \text{ \AA.}$ in

S.G.V.

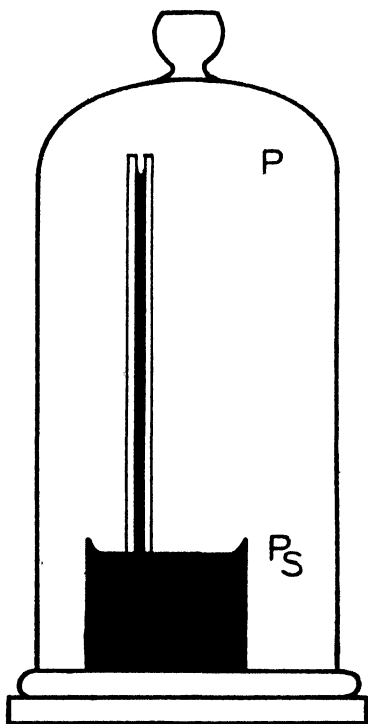


Fig. 131.—Rise of Liquid in a Capillary Tube showing that Vapour Pressure is less at a Concave Meniscus by an amount equal to the Weight of the Column of Vapour.

F F

radius. If $p/p_s = 0.1$, the radius of the largest pores in which water could condense would be about $4.6 \text{ \AA.}$, a numerical deduction which becomes meaningless when it is recalled that this is already down to molecular dimensions.

TEST OF THE CONSTANCY OF PORE VOLUME DEDUCED

An essential corollary of the capillary condensation hypothesis is that the same specimen should sorb the same volume of various liquids independent of their chemical nature.¹ This requirement appears to be satisfied for the original silicic acid jellies used by Zsigmondy and Anderson.² At the special point "O" of his silicic acid, Anderson found that the effective radius of the pores calculated for the amounts of water, alcohol and benzene taken up in separate experiments was 27, 26, and 30 $\text{\AA.}$, respectively, which still appears not only plausible but probable. Patrick (loc. cit.) deduced from his experiments with sulphur dioxide at 0° a similar diameter but stated that at 15° the numbers so obtained (such as $0.8 \text{ \AA.}$ for values of the sorption, x/m , at 15° , exceeding the amount of sorption at 0° for which the capillary radius, obtained by calculation, was 24 $\text{\AA.}$) were impossible and would demand an extension of the capillary hypothesis.

McGavack and Patrick³ have presented experiments with silica gel and sulphur dioxide in which sorption and desorption curves coincide if air is eliminated. The results, like those in Patrick's *Dissertation*, show fair agreement with the "exponential" formula (see fig. 3, *J. Am. Chem. Soc.*, 1920, **42**, 954), the value of $1/n$ ranging from 0.745 at 100° to about 0.4 at -80° . When the results for all pressures and temperatures are plotted on one graph against the values of the relative pressures, p/p_s , it is found that the volume sorbed (calculated as liquid) tends to be independent of the tempera-

¹ This has been shown by J. W. McBain, H. P. Lucas and P. F. Chapman (*J. Am. Chem. Soc.*, 1930, **52**, 2668) not to be the case for toluene and acetic acid with charcoal.

² J. S. Anderson, *Dissert.*, Göttingen, 1914; *Z. physik. Chem.*, 1914, **88**, 191.

³ J. McGavack Jr. and W. A. Patrick, *J. Am. Chem. Soc.*, 1920, **42**, 946.

ture as p/p_s approaches unity. However, the results for the lowest values of p/p_s differ by several fold when compared at the two extremes of temperature. McGavack and Patrick, like Patrick in 1914, consider that, owing to the curvature of the meniscus at the exposed end of the capillary, the liquid is under a negative hydrostatic pressure of the order of 500 atmospheres.¹ Modifying a suggestion that in some cases the compressibility (and, therefore, extensibility) is proportional to the surface tension raised to a fractional power,² they find it possible to express all their results for sulphur dioxide sorbed by silica gel at various temperatures by the formula,

$$V = 0.1038 \left(\frac{p}{p_s} \right)^{0.477}.$$

They state: "this is strong evidence of our claim that the volume occupied by the adsorbed vapour is the same at the same value of the corresponding (relative) pressure, p/p_s ". We shall see later that several other formulæ, based on wholly different conceptions, express these results quite as well. This proves only that the phenomena of sorption are subject to very general laws. It should be borne in mind that the form, number and distribution of capillary spaces and pores in their silica gel are all unknown and that the success of the equation is just that by suitable arbitrary choice of the constants it may be fitted to the facts. Moreover, the capillary condensation hypothesis may be tested in other ways.

McGavack and Patrick state:

"It is our belief that the adsorption of gases or vapours, let us say at all temperatures below the critical temperature, may

¹ W. A. Patrick and C. E. Greider (*J. Phys. Chem.*, 1925, **29**, 1031) found that the heat of wetting of silica gel at 0° C. is positive. Hence, since this is below the temperature of maximum density of water, it follows from Le Chatelier's principle that either there is no compression or that the compression is so enormous as to have brought the temperature of maximum density below 0° C.

² For a criticism of this empirical formula and the theory upon which it is based, see S. J. Gregg, *J. Phys. Chem.*, 1928, **32**, 616.

be predicted from a knowledge of the physical constants of the gas or vapour alone. Furthermore, the rôle of the adsorbent is simply that of a porous body, its chemical nature being a matter of indifference. (Cases of obvious chemical affinity are of course excluded.)”

There are two essentials in this hypothesis. First, that a given specimen of a porous body should sorb equal volumes

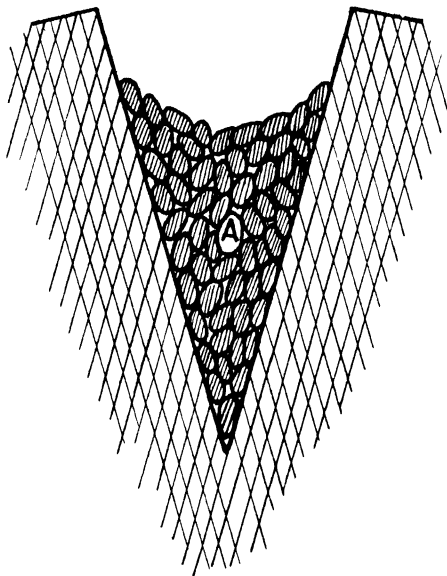


Fig. 132.—V-shaped Pore filled at given Relative Humidity to definite Diameter and Concavity of Meniscus by Liquid condensed in Bulk.

of all liquids which wet it. Second, that each molecule of condensed liquid is surrounded by like molecules, well out of reach of any specific influence of the molecules of the solid walls. This is illustrated by the accompanying diagram, fig. 132, which represents a V-shaped pore full of elliptical molecules, forming a concave meniscus, where, for example, the molecule marked *A* is completely surrounded by other liquid molecules.

The first postulate does in fact correspond to the rough empirical rule that approximately equal volumes of liquid are sorbed from various vapours which are nearly at the saturation pressure and at the same temperature. For example, Gurwitsch,¹ quoted *in extenso* by Langmuir,² showed that 1 gm. of fuller's earth exposed to *saturated* vapours of various liquids took up a volume ranging between 0.610 c.c. for benzene to 0.684 c.c. for acetone. Coolidge,³ using various liquids, found that 1 gm. of charcoal at pressures approaching but not quite equal to the saturation vapour pressure sorbed between 0.424 c.c. with water and 0.494 c.c. with ether. Incidentally, these amounts are approximately parallel to the compressibility of the respective liquids.

Coolidge used his data to test the capillary condensation hypothesis as follows :

"When at 0°, enough benzene has been adsorbed to fill a space of 0.02 c.c. with subcooled liquid at normal density (about half the ultimate capacity), the pressure of the system is 0.0055 mm., so that $-\log p/p_s = 3.68$. Taking $\sigma = 32$ and $v = 86.9$, we get $r = 2.89 \times 10^{-8}$ cm. Overlooking the fact that this radius is already of molecular magnitude, let us use it to predict the relative pressure under different conditions, but always with enough vapour adsorbed to fill 0.2 c.c. with normal liquid at the temperature in question.

Substance	Ben- zene	Ben- zene	Carbon disulphide	Ether	Water
Temperature, ° C.	99	150	0	0	0
— $\log p/p_s$, calculated	1.82	1.19	2.65	2.51	1.80
— $\log p/p_s$, observed	2.74	2.44	2.60	4.0	0.26

"It has been supposed that the capillary condensation theory under discussion may hold better in the case of inert adsorbents like silica gel. Suitable data for a test are given by McGavack and Patrick.⁴ Interpolating from their fig. 8, we find for a

¹ L. G. Gurwitsch, *J. Russ. Phys.-Chem. Soc.*, 1915, **47**, 805.

² I. Langmuir, *J. Am. Chem. Soc.*, 1917, **39**, 1898.

³ A. S. Coolidge, *J. Am. Chem. Soc.*, 1924, **46**, 596; critical discussion of this and other sorption hypotheses, 1926, **48**, 1795.

⁴ J. McGavack Jr. and W. A. Patrick, *J. Am. Chem. Soc.*, 1920, **42**, 946.

volume of 0.1 c.c. of sulphur dioxide at 0°, that $-\log p/p_s = 1.54$, whence, using their data for σ and v , r is found to be 3.16×10^{-8} . On this basis, the calculated relative pressures should, at -80° and at 100° , have the negative logarithms 2.99 and 0.47, instead of the observed 1.71 and 1.16, always for 0.1 c.c. of liquid sulphur dioxide."

Wilson¹ points out that discrepancies of many fold arise if the sorption of oxygen and nitrogen by the same charcoal is ascribed to capillary condensation.

THE VERY LOW VALUES DEDUCED FOR CAPILLARY RADII

The most serious discrepancy between formulation and experiment is in the actual values for the radius of the exposed end of the capillaries as calculated from the relative vapour pressure by the Thomson equation. The preceding quotation from Coolidge gives two instances of values of r equal to 3 Å., whereas a molecule such as carbon tetrachloride has a diameter of about 3.6 Å., and the benzene molecule has a width of 6.2 Å. Examining the data of McGavack and Patrick for sulphur dioxide, in their silica gel it is found that for 10, 30 and 50 per cent of the total maximum amounts which can be sorbed the values of r would be 1, 4 and 7 Å., respectively. Similar calculations from heat of sorption (private communication from Professor J. H. Hildebrand) give even smaller values for r .

This difficulty is very greatly intensified by the fact that with well evacuated charcoal most of the sorption of vapours occurs at pressures amounting to only a few hundredths of the saturated vapour pressure at that temperature.² In several cases it was found by the author and his collaborators that the sorption is only halved when the pressure is but 1/10,000 of saturation.

Fleischer³ has calculated the largest pores in any porous body which could be filled at various relative pressures

¹ R. E. Wilson, *Phys. Rev.*, (2), 1920, **16**, 14.

² J. W. McBain, H. P. Lucas and P. F. Chapman, *J. Am. Chem. Soc.*, 1930, **52**, 2675; J. W. McBain, D. N. Jackman, A. M. Bakr and H. G. Smith, *J. Phys. Chem.*, 1930, **34**, 1439.

³ A. Fleischer, *Am. J. Science*, 1928, **16**, 247.

(relative humidities, p/p_s) for water, methyl alcohol, benzene and diethylamine. His calculated results are given in table 55 which shows that only at fairly high relative pressures will capillary condensation be possible in pores greatly exceeding molecular dimensions. These values, as Zsigmondy emphasized, are not the total radii, $2r$, of the pores but $2r - 2x$, where x is the thickness of the adsorbed layer.

TABLE 55

Minimum Relative Pressures at which Capillary Condensation of Typical Liquids can occur in Pores not exceeding given Dimensions

r in Å.	1,000	750	500	250	100	50	30	20	10
H ₂ O	0.991	0.987	0.98	0.961	0.903	0.816	0.712	0.601	0.362
CH ₃ OH	0.995	0.992	0.986	0.973	0.928	0.862	0.780	0.690	0.473
C ₆ H ₆	0.981	0.975	0.962	0.926	0.824	0.679	0.526	0.381	0.145
(C ₂ H ₅) ₂ OH	0.976	—	0.970	—	0.858	0.738	—	—	0.219

It is evident that the requirements illustrated in fig. 132 are not in accordance with the facts. The molecules of sorbed material are in direct contact with the solid sorbent instead of being surrounded by like molecules of liquid. Even a protest that r cannot be so calculated because the surface tension may have been radically changed is but to admit that the molecules of liquid are within the range of influence of the molecules of solid; and this effectively replaces capillary condensation by sorption on a surface.¹

OTHER EVIDENCE AGAINST CONDENSATION AS A GENERAL EXPLANATION OF SORPTION

Bangham and Fakhoury,² who found that charcoal expands in proportion to the square of the amount of material sorbed upon it, point out that this does not agree with the conception of sorption as capillary condensation.

Capillary condensation could not in itself serve as a general explanation of sorption because it leaves out sorption on

¹ An inconclusive attempt to determine the state of carbon disulphide and of propyl alcohol sorbed by coconut charcoal through examination by X-rays has been made by M. Hirata (*Proc. Imp. Acad. (Japan)*, 1929, 5, 450).

² D. H. Bangham and N. Fakhoury, *Nature*, 1928, 122, 681.

plane surfaces and sorption of gases. Patrick's attempt ¹ to take it literally for sorption from solutions is curiously forced. There is in fact no demonstrable difference in behaviour or kind between the sorption of a vapour such as nitrous oxide and a permanent gas such as nitrogen, which have both been studied at room temperature with sugar charcoal by Dr. G. T. Britton in the author's laboratory at the University of Bristol up to a pressure of 60 atmospheres. (See Chapter IV, page 110.)

Another reason sufficient in itself for the rejection of capillary condensation as a general hypothesis is its total inadequacy to explain such phenomena as the following :

(1) Bangham and Stafford ² found that if graphite is made the cathode for the passage of the high tension discharge through hydrogen, much hydrogen is absorbed, and this appears to be chemically bound to the carbon. The graphite now displays considerably enhanced activity towards oxygen, the increase being proportional to the amount of added hydrogen. No water is eliminated, either during the hydrogen absorption or on the subsequent exposure to oxygen. The suggestion is made that the absorption of hydrogen effects similar changes of properties to those which accompany the reduction of benzene to dihydrobenzene. The sorption of oxygen both by the original and by the hydrogen-treated graphite appeared to be exactly similar in type to that of ammonia, carbon dioxide, nitrous oxide, etc., on glass. Further, the hydrogen had little influence upon the sorption of carbon dioxide.

(2) The phenomena exhibited in the sorption of oxygen and other substances by charcoal differ greatly at different temperatures. See, for example, the description in Chapter I.

CASES WHERE CAPILLARY CONDENSATION UNDOUBTEDLY OCCURS IN ADDITION TO SORPTION

The rejection of the capillary condensation hypothesis as an explanation of sorption is not to deny that such con-

¹ W. A. Patrick and D. C. Jones, *J. Phys. Chem.*, 1925, **29**, 1.

² D. H. Bangham and J. Stafford, *J. Chem. Soc.*, 1925, **127**, 1085.

densation must occur when pores, capillaries and cavities of suitable dimensions are exposed to the nearly saturated vapours of liquids which wet them. For example, it is probable that Zsigmondy and Bachmann are correct in ascribing the opacity which occurs in silicic acid jellies, particularly when aged, upon exposure to a certain range of vapour pressure, to the filling and emptying of pores or patches¹ by liquid condensed in bulk. In the first place, with the gels made by them, pronounced hysteresis was observed in the region in question. In the second place, the diameters of the pores in their gels, as calculated from the observed pressures, are of the highly plausible order of magnitude of 50 to 60 Å. for such different liquids as water, alcohol and benzene. Even here, however, in view of the very appreciable sorption at lower pressures, it seems advisable to adhere to Zsigmondy's original view, that the particles forming the structure of the silicic acid are each covered with an adsorbed film and that the diameters of pores indicated correspond to the distance between neighbouring films. The structure of McGavack and Patrick's silica gel probably differs from those of Zsigmondy, Bachmann and van Bemmelen² in containing no such pores; see Bray and Draper.³

To sum up, the quantitative treatment of the capillary condensation hypothesis leads to its rejection on the ground that the sorbed molecules are evidently within the range of influence of the molecules of solid. The re-interpretation of the data may rather be used to throw light upon the structure of the solid sorbent.

Bray and Draper found for the sorption of water by partially hydrated oxides of copper, manganese and their mixtures results similar to those obtained by Lowry and Hulett⁴

¹ Patches of gel, not necessarily empty, see page 182.

² J. M. van Bemmelen, *Z. anorg. Chem.*, 1897, **13**, 233; 1898, **18**, 14.

³ W. C. Bray and H. D. Draper, *Proc. Nat. Acad. Sciences*, 1926, **12**, 295. See also H. D. Draper (*J. Am. Chem. Soc.*, 1928, **50**, 2637) for a discussion of the distinction between pore volume and amount of water adsorbed in these oxides.

⁴ H. H. Lowry and G. A. Hulett, *J. Am. Chem. Soc.*, 1920, **42**, 1393.

with various gas-mask charcoals and by Munro and Johnson¹ with alumina. They found a rapid increase of sorption at higher vapour pressures which, as shown by the Göttingen school,² is attributable to condensation of liquid in capillaries. Bray and Draper's data for copper oxide are twice plotted in fig. 133.³ On the left side of the diagram x/m is plotted against pressure, and it is seen that there is a point of inversion on the sorption curve at F, where the capillary condensation begins to be appreciable. The value of the radius, r , of the pores at this point is calculated as 15 Å. and at the point B for $p/p_s = 0.93$ as 150 Å. It is considered that the sorption proper is represented by the curve GF continued by the dotted line to H and that the capillary condensed water is that shown above the dotted line. On the right of the diagram the same data are plotted with the co-ordinates of the Williams-Henry formula. An approximately straight line is actually obtained between G and F, but beyond that point there is a complete reversal in the direction of the curve FB due to the water condensed in bulk.

Neglect of the possibility or probability of capillary condensation leads to serious errors in work where suitable capillaries are present, as for example, in the study of powders or textiles or glass wool. Katz⁴ studied excessively fine powders of quartz and anorthite containing about 10^{11} particles per gram. His curves for the sorption of water vapour are somewhat similar to those of Bray and Draper, fig. 133, and it is evident that, where the relative humidity exceeded 80 or 90 per cent, capillary condensation occurred. The previous parts of Katz's curves obey the Williams-Henry formula with a reversal of direction where the relative humidity approaches saturation.

¹ L. A. Munro and F. M. G. Johnson, *J. Phys. Chem.*, 1926, **30**, 172.

² W. Bachmann, *Z. anorg. allgem. Chem.*, 1913, **79**, 202; 1917, **100**, 1.

³ W. C. Bray and H. D. Draper, *Proc. Nat. Acad. Sciences*, 1926, **12**, 297.

⁴ J. R. Katz, *K. Akad. van Wetenschappen, Amsterdam, Proc. Sec. of Sciences*, 1912, **15**, 445.

When the liquid wets the solid, capillary condensation may be expected to set in as soon as the pressure of the

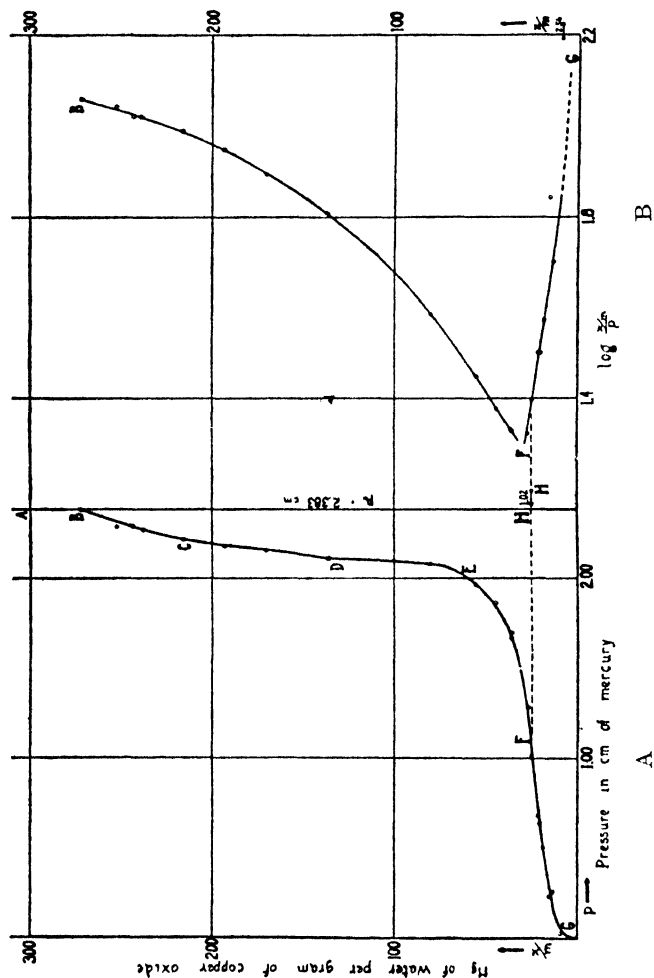


Fig. 133.—A—The Sorption Isotherm for Water on Copper Oxide at 25°C.; B—The variation of x/m with $\log \frac{p}{p_s}$ (Williams-Henry Equation).

vapour approaches saturation, since some pores are almost always present. In this region the values for sorption and desorption may not always be reproducible, owing to such

factors as "friction" in the contact angle and hysteresis in wetting. If wetting does not occur, the sorption should be reproducible right up to or even beyond the saturation pressure. Photography by the old daguerreotype process depended upon mercury wetting only the illuminated portions of a plate covered by silver iodide.

INFLUENCE OF THE NEIGHBOURHOOD OF SURFACES UPON LIQUIDS

In later attempts to maintain their special point of view, Patrick and his collaborators have concluded that the properties of matter in pores are greatly altered from those usually observed. For example, Patrick, Preston and Owens,¹ on obtaining no break on the sorption curves for carbon dioxide and nitrous oxide with silica gel between 30° and 40°, conclude that "the critical temperature is raised, and that condensation and surface tension exist even at 40°". Similarly, Patrick and Eberman² suppose that another physical constant, the surface tension, is much greater in capillaries. A direct attempt to demonstrate this was made by Shereshefsky³ in tubes of 1 to 6×10^{-4} cm. diameter. However, such measurements are subject to a number of sources of error, and, more especially, his method of estimating the diameter of such fine capillaries by mere observation with a microscope, the side of the tube acting as a cylindrical lens, is inadequate.

The author is of the opinion that water in the neighbourhood of a surface is not in the ordinary liquid form but is subject to the influence of that surface.⁴ The first monomolecular layer of molecules is completely held and polarized by the solid surface. Other molecules will become attached

¹ W. A. Patrick, W. C. Preston and A. E. Owens, *J. Phys. Chem.*, 1925, **29**, 421.

² W. A. Patrick and N. F. Eberman, *J. Phys. Chem.*, 1925, **29**, 220.

³ J. L. Shereshefsky, *J. Am. Chem. Soc.*, 1928, **50**, 2966, 2980.

⁴ J. W. McBain and G. P. Davies, *J. Am. Chem. Soc.*, 1927, **49**, 2230; J. W. McBain, *Nature*, 1927, **120**, 372; J. W. McBain and R. DuBois, *J. Am. Chem. Soc.*, 1929, **51**, 3534.

to this polarized surface and form chains of polarized molecules extending far into the liquid. In the particular case under discussion, where the walls of the capillary are close together, most of the water might well be in this condition as is indicated in fig. 134. The water as so portrayed might very possibly have a lower vapour pressure than water in bulk,

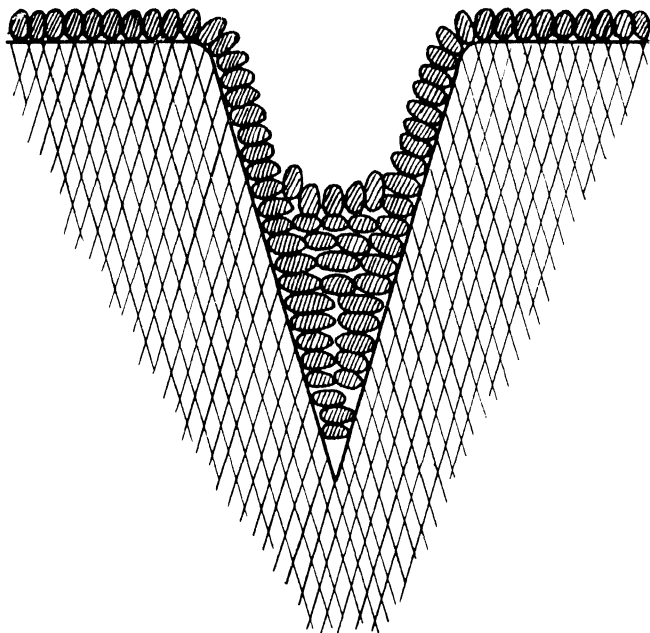


Fig. 134.—V-shaped Pore showing Monomolecular Sorbed Layer and Chains of Polarized Molecules reaching between the Walls.

even with similarly curved surface; but we have departed from the hypothesis of mere capillary condensed water, which was the subject of this chapter, and have gone over to the hypothesis of polymolecular sorption discussed in Chapter XVIII under the title of laminated or enchainned multimolecular films.

Finally, it follows incidentally from the foregoing discussion of the hypothesis of capillary condensation that great doubt

is cast upon the usual areas calculated for the surface of such porous bodies as gas-mask charcoal. The basis of the commonly quoted figures is this discredited hypothesis, assuming sorption proper to be negligible. The error is presumably worse if adsorption can be multimolecular. Again, the calculation is usually based upon the sorption of water, which in the case of charcoal is especially subject to error and is often anomalous (see Chapter IV, page 143).

CHAPTER XVII

THE CLASSICAL HYPOTHESIS OF A THICK COMPRESSED FILM

Whereas in the capillary condensation hypothesis it was assumed that each sorbed molecule was surrounded and held by like molecules, the sorbent supplying merely an indifferent solid framework, the essential conception in the hypothesis of a compressed film, propounded by de Saussure in 1814, is that molecules coming near the surface of a solid sorbent are strongly attracted towards it. In effect this assumes a large range of molecular attraction and postulates such attraction between unlike molecules. The interaction between like molecules is revealed in such phenomena as condensation of vapours to liquids, surface tension, and heat of vaporization; and is expressed, for example, by the constant a in van der Waals' equation $(p + a/v^2)(v - b) = RT$. It is likewise involved in the hypothesis of the multimolecular film.

By virtue of the attraction towards the solid surface the gas or vapour in its neighbourhood is assumed to be under enormous pressure of the order of magnitude of at least 34.4 atmospheres (Mitscherlich, 1843), 6,150 atmospheres (Chappuis, 1880), 100 atmospheres (Bunsen, 1881), 240 atmospheres (Müller-Erbach, 1886) 10,000 atmospheres (Lagergren, 1898), 5,000 atmospheres (Polányi, 1916), 10,000 atmospheres (Williams, 1919), 12,000 atmospheres (Harkins and Ewing, 1921), 37,000 atmospheres (Lamb and Coolidge, 1920), or 5,000 atmospheres (Bartell and Osterhof, 1928), falling off with increasing distance from the solid surface. Hence, extending out from the surface of the solid there is a sorption region whose outer limit is determined by the distance at which the attraction towards the solid becomes inappreciable. Within this sorption region the gas or vapour will therefore

assume a density and state of aggregation in accordance with its equation of state. For example, a nearly saturated vapour would certainly be compressed to a liquid within the sorption region. This is indicated in curve *I* of fig. 135 taken from

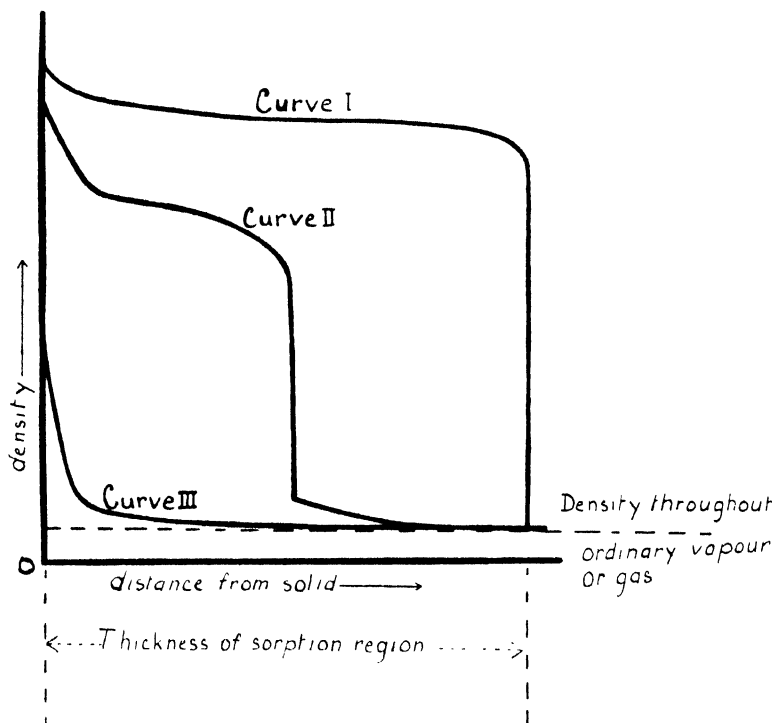


Fig. 135.—The Density of the Sorbed Material in the Sorption Region as compared with the Density in the Bulk of the Gas or Vapour.

Lowry and Olmstead.¹ In this case the sorption region is full of liquid and appears fairly sharply defined at its external boundary. The other extreme is represented by curve *III* for a gas under low pressure where there is practically no excess of gas and, therefore, no adsorption in the outer part of the sorption region but only a small amount of compressed gas (not

¹ H. H. Lowry and P. S. Olmstead, *J. Phys. Chem.*, 1927, **31**, 1605.

liquid) in the immediate neighbourhood of the solid surface. Their curve *II* is an intermediate case such as is supposedly obtained at ordinary temperature and pressure with carbon dioxide. Such cases are very clearly pictured, for example, by Bunsen ¹ in discussing his experiments with carbon dioxide and glass. Dewar ² quotes Mitscherlich's ³ calculations of de Saussure's measurements of the sorption of carbon dioxide by charcoal at 12° C. upon this basis. In successive layers within

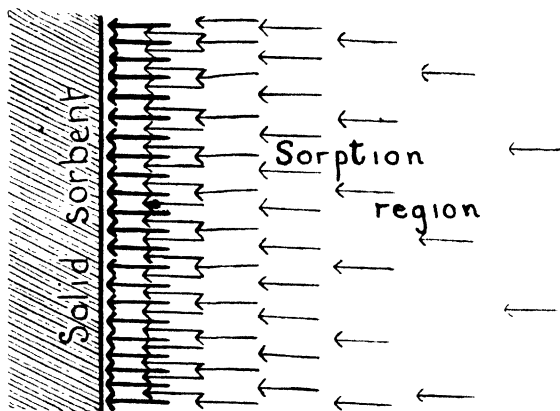


Fig. 136.—Diagram to represent Hypothetical Attractive Forces in the neighbourhood of a Solid, indicating that they are greatest and that they cause greatest compression of the Sorbed Material in the immediate neighbourhood of the Surface, and that they decrease to negligible Values at a certain distance from the Surface, the space between being called the Sorption Region.

the sorption region the vapour is at first compressed until its saturated vapour pressure is reached, whereupon all layers underneath must be liquefied, and in the immediate neighbourhood of the solid even the liquid is under strong compression. According to van der Waals, the density at infinite compression would reach the value $M/22412b$.

The diagrams in figs. 136 and 137 portray the conditions in

¹ R. W. Bunsen, *Wied. Ann. der Physik*, 1883, **20**, 545.

² J. Dewar, *Proc. Roy. Inst. Gt. Britain*, 1905, **18**, 180.

³ M. E. Mitscherlich, *Taylor's Scientific Memoirs*, 1846, **4**, 3; from *Ann. chim. phys.*, (3), 1843, **7**, 15.

the thick compressed film. The former shows by arrows, graduated in numbers and in thickness, the strong forces and high compression in the immediate neighbourhood of the solid and their falling off with distance. Polányi's¹ diagram (fig. 137) shows for a rough surface the lines of equipotential or equal compression in the sorption space between the uniform gas space and the solid surface. According to Müller-Erzbach,²

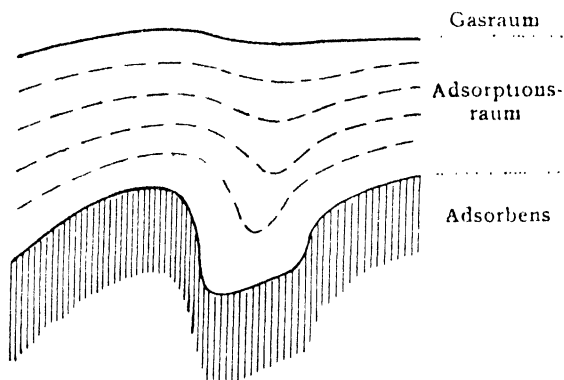


Fig. 137.—Polányi's Diagram of the Sorption Region, showing levels of Equal Adsorption Potential.

the vapour tension of the first two layers falls off with the inverse twenty-sixth and that of the outermost layers with the inverse fourth power of the distance from the solid surface.

QUANTITATIVE FORMULATION OF THE COMPRESSED FILM HYPOTHESIS

The quantitative formulation of this hypothesis is largely due to Eucken³ and Polányi.⁴ Polányi lists the assumptions in this potential theory of adsorption as follows:

¹ M. Polányi, *Z. Elektrochem.*, 1920, **26**, 371.

² W. Müller-Erzbach, *Wied. Ann. der Physik*, 1886, **28**, 684.

³ A. Eucken, *Verh. deut. physik. Ges.*, 1914, **16**, 345.

⁴ M. Polányi, *Verh. deut. physik. Ges.*, 1914, **16**, 1012; 1916, **18**, 55; *Magy. chem. Foly.*, 1917, **23**, 33, 49, 65; *Z. Elektrochem.*, 1920, **26**, 370; *Festschrift Kaiser Wilhelm Ges. Förderung Wiss. Zehnjährigen Jubiläum*, 1921, p. 171; *Z. Elektrochem.*, 1922, **28**, 110; L. Berényi,

- (1) The adsorption potential and the forces involved are independent of the temperature.
- (2) The adsorption potential ¹ at a given point is independent of the presence or absence of other molecules around it in the sorption space or between it and the solid, whether these are molecules of like kind or not. In other words, each arrow in fig. 136 represents an attraction inherent in that position, independent of the presence or absence of other molecules in the positions occupied by the other arrows.
- (3) The van der Waals' forces, or forces of cohesion, are unaffected by the sorption so that the ordinary equation

Z. physik. Chem., 1920, **94**, 628; 1923, **105**, 55; *Z. angew. Chem.*, 1922, **35**, 237; H. H. Lowry and P. S. Olmstead, *J. Phys. Chem.*, 1927, **31**, 1601. For a theoretical discussion of the attractive and repulsive forces acting upon a sorbed layer, see P. G. Nutting, *J. Wash. Acad. Sci.*, 1929, **19**, 295.

¹The formulation of "adsorption potential", as used by earlier investigators of the subject of capillarity, such as Lord Rayleigh and van der Waals, was at the latter's suggestion applied to sorption by J. R. Katz (*Proc. Acad. Sci. Amsterdam*, 1912, **15**, 445; *Chem. Ztg.*, 1912, **36**, 607). It is defined as the work required to bring a molecule from anywhere in the homogeneous gaseous phase to a state similar to that in which it exists at a given position in the neighbourhood of the solid. In calories per gram mol it is the energy required to compress a gram mol of gaseous atmosphere to the density equal to that at which it is found at a given point within the sorption region. For a vapour, $\epsilon = RT \ln p/p_s$ is the adsorption or sorption potential or the work required to bring one gram mol from the liquid whose vapour pressure is p_s into the sorption region which is in equilibrium with a vapour at pressure p ; this formula also was suggested to Katz by van der Waals in 1912.

$$\text{For a gas } \epsilon = \int v = \frac{M}{\delta} \quad v.dp = g(\delta), \text{ where } x \text{ is the amount}$$

$$v_x = \frac{RT}{p_x}$$

of sorption, v is the molecular volume of the adsorbed gas at the given point under consideration, δ being its density and M the molecular weight; p_x is the pressure in the homogeneous gaseous phase and v_x is the molecular volume in that phase.

of state will apply even within the sorbed layer. This assumption was made explicit by Polányi but was used by the earlier workers, such as, for example, Mitscherlich (*loc. cit.*).

Polányi's distinctive contribution is the suggestion that, since the attractive influence of the solid is assumed to be independent of the temperature, one experimentally determined isotherm can be made use of in predicting the others for the same system by merely applying the equation of state. This is very useful in testing the hypothesis, because in general, the surface of the sorbing solid, the range of molecular attraction, and the laws according to which the attracting forces fall off with the distance from particular points on the surface of the sorbing solid, are all unknown.

Polányi's first attempts in this direction were improved by Berényi,¹ who recalculated many of the results in the literature, such as those of Titoff, Homfray, Richardson, Patrick, Berl and Andress, for gases and vapours by charcoal and silica gel. He proceeds by calculating the adsorption potential as a function of the amount adsorbed. The sorption region is assumed invariable, independent of temperature, whereas the material within it has a density depending upon its compressibility and its expansion with temperature. The volume of the sorption region has to be estimated by some such device as that of taking the actual amount of sorption at a temperature well below the critical temperature and at a pressure approaching the vapour tension of the liquid whose vapour is being sorbed; it is thereupon assumed that the whole of the sorption region is filled with the liquid, and its volume is determined by dividing the amount of that liquid by its ordinary density at that temperature and at only atmospheric pressure. To be sure, this neglects the decrease in volume of the liquid under the enormous pressures assumed to obtain in the sorption region. For example, Lamb and Coolidge estimated that 0.4 c.c. of liquid carbon disulphide must be

¹ L. Berényi, *Magy. chem. Foly.*, 1919, **25**, 109; *Z. physik. Chem.*, 1920, **94**, 628; 1923, **105**, 55.

compressed into 0.25 c.c. of sorption region on charcoal under an attractive pressure of 37,000 atmospheres.

Similarly, the volume occupied by the liquefied vapour at lower relative humidities may be plotted against the adsorption potential calculated from those relative humidities. If ϕ is the volume filled with liquid between the surface and one of the positions of constant potential represented by the broken lines in fig. 137, then $\phi = x/\delta_r$ and $\varepsilon = f(\phi)$, where δ_r is the density of the liquid at temperature T . For calculating the values of ε and ϕ at temperatures not so far below the critical temperature, van der Waals' equation is utilized and corrections have to be made for the varying values of the density within the film. The second step is the calculation of the function $\varepsilon = g(\delta)$ by using the equation of state, and the third step consists of the determination of the function $\delta = h(\phi)$, where p_x and T are again constant. This is obtained by the elimination of ε between the equations $\varepsilon = g(\delta)$ and $\varepsilon = f(\phi)$; the former changes with p_x and T , whereas the latter is assumed invariant for all temperatures. Hence the function $\delta = h(\phi)$ is different for each value of p_x and T . If it is known for a given temperature and a given p_x , x may be calculated by the integral $x = \int_{\phi=0}^{\phi=\phi_m} \delta \cdot d\phi$, where ϕ_m is the maximum volume indicated by the continuous line in fig. 137. To obtain x , Berényi plotted δ as a function of ϕ , measuring with a planimeter the area bounded by the curve, the two axes and the ordinate for $\phi = \phi_m$.

CHARACTERISTIC CURVE OF ADSORPTION

Berényi thus obtained empirical curves for the isotherms connecting adsorption potential with a corresponding volume of sorbed material. He found that for a series of isotherms of any one substance with a particular solid, all these curves more or less coincided. This is called the characteristic curve of adsorption. Taking a mean value from the superimposed curves, he calculated back again to what the observed points ought to have been to satisfy his calculations exactly. An impression is given of the degree of success in thus correlating

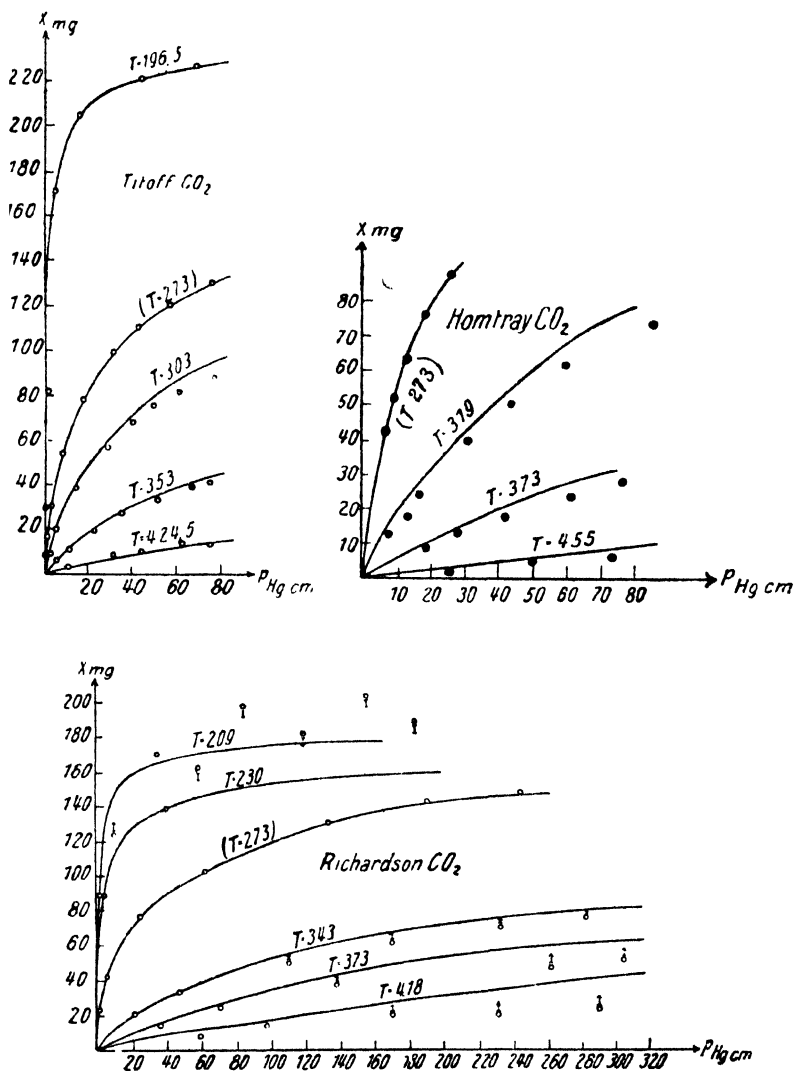


Fig. 138.—Berényi's Comparison of Observed Data (points) with the family of Curves obtained from Polányi's Formulation after assuming one Isotherm in each Case.

the data on the semi-empirical basis by the typical diagrams, fig. 138,¹ for the sorption of carbon dioxide by charcoal in the experiments of Titoff, Miss Homfray and Richardson. The

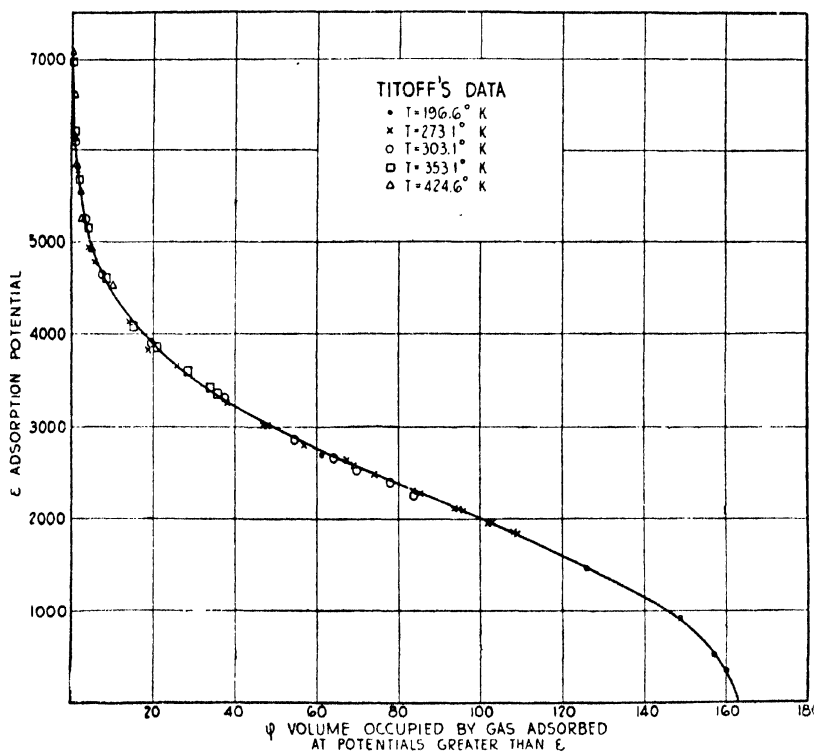


Fig. 139.—Lowry and Olmstead's Reduction of Titoff's Data for the Sorption of Carbon Dioxide by Charcoal to one characteristic Curve.

curves, drawn in full, are those finally calculated; the points are the actual experimental data.

Noteworthy success in this direction has been achieved by Lowry and Olmstead² who have recalculated the more careful determinations of the sorption of carbon dioxide by charcoal.

¹ L. Berényi, *Z. physik. Chem.*, 1920, **94**, 640, figs. 2, 3 and 4.

² H. H. Lowry and P. S. Olmstead, *J. Phys. Chem.*, 1927, **31**, 1601.

They used the values of pv as a function of p and T given in standard tables supplemented by van Laar's more precise extension of the van der Waals equation. Some of the characteristic curves at which they arrive are shown in figs. 139, 140 and 141.

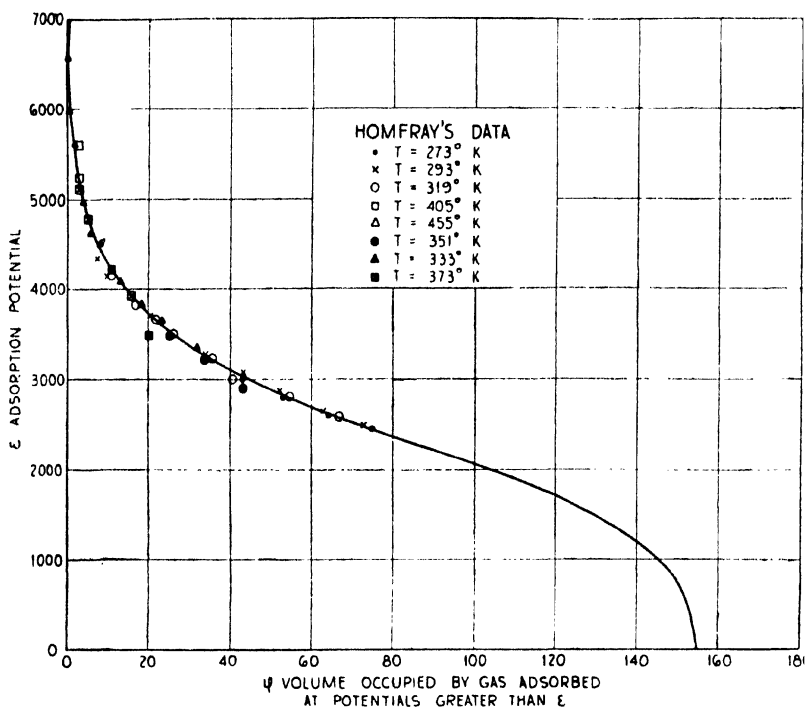


Fig. 140.—Lowry and Olmstead's Reduction of Homfray's Data for the Sorption of Carbon Dioxide by Charcoal to one characteristic Curve.

The least that can be said in view of such numerical successes is that the physical type of sorption is subject to very general laws such as govern cohesion in general. Any connexion with surface tension, van der Waals' coefficient, condensability or solubility involves each of the others and related general properties.

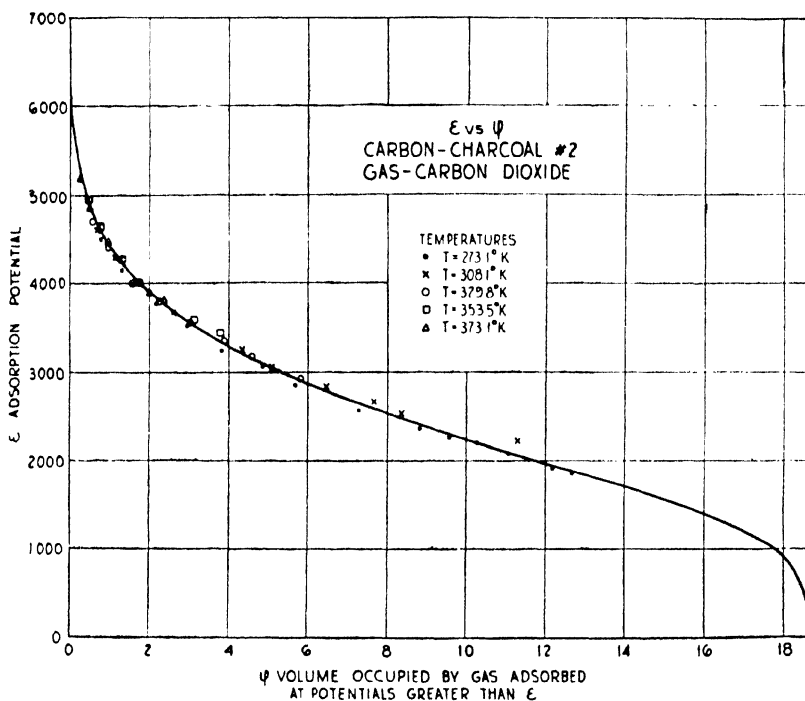


Fig. 141.—Lowry and Olmstead's Reduction of Morgan's Data for the Sorption of Carbon Dioxide by Charcoal to one characteristic Curve.

RELATION BETWEEN ADSORPTION POTENTIAL AND VAN DER WAALS' CONSTANT a

Polányi¹ points out that the characteristic curves for various gases and vapours sorbed by the same charcoal are not only similar in form (as they must be, since sorption curves in general are similar), but also that the adsorption potential near the solid is proportional to the square root of a , the attraction coefficient of van der Waals' equation, for the respective gases; his calculations are given in table 56 where ϵ_m is the adsorption potential.

¹ M. Polányi, *Z. Elektrochem.*, 1920, **26**, 372.

TABLE 56

Polányi's Comparison of Adsorption Potential with the Square Root of van der Waals' Coefficient a

Substance Sorbed	ϵ_m in cal.	$10^3\sqrt{a}$	$\frac{\epsilon_m}{\sqrt{a}}$
Ethylene	7.10	94.1	75
Carbon dioxide	6.10	84.7	72
Methane	5.23	60.8	86
Carbon monoxide	4.84	53.0	91
Oxygen	4.45	51.9	86
Nitrogen	4.32	51.8	83
Argon	4.10	51.0	80
Hydrogen	about 3	20.6	150

This relation confirms the suggestion of Prince Galitzine,¹ Berthelot² and others that molecular attraction between unlike molecules should be proportional to the square roots of their respective van der Waals' coefficients, $\sqrt{a_1}, \sqrt{a_2}$. According to this, the forces are completely unspecific, since a molecule enters, with the same value for its own $\sqrt{a}$, into its relations with every other kind of molecule. It is significant, as pointed out by Eucken,³ that the characteristic curves as calculated by Berényi for molecules which are permanent dipoles and for those which have no electric moment are indistinguishable (see Chapter XX).

RECENT DEVELOPMENTS AND MODIFICATIONS OF THE COMPRESSED FILM THEORY

A more recent development of the potential theory is the attempt to harmonize it with the present-day assumption that forces between molecules are of short range. Polányi⁴ points out that in the assumptions listed above there is no explicit statement as to the thickness of the film, which might still be only one molecule deep. Eucken,⁵ indeed, from calcula-

¹ Prince B. Galitzine, *Wied. Ann. der Physik*, 1890, **41**, 770.

² D. Berthelot, *Compt. rend.*, 1898, **126**, 1704.

³ A. Eucken, *Z. Elektrochem.*, 1922, **28**, 11, 257.

⁴ M. Polányi, *Z. Elektrochem.*, 1929, **35**, 431.

⁵ A. Eucken, *Verh. deut. physik. Ges.*, 1914, **16**, 345

tions assuming that molecular attraction falls off as the inverse fourth power of the distance and comparing calculated with observed results, concluded that most of the sorbed molecules must be in actual contact with the solid. Later ¹ he calculated that the centres of all sorbed molecules must lie within a layer between 0.7 and 1.5 of a molecular radius deep. His calculations of heat of sorption agreed in magnitude with the observed heat of sorption. In 1922 Eucken ² expressly renounced the claims of the potential hypothesis in favour of the Langmuir conception.

In 1928 Polányi ³ explicitly modified his compressed film theory by making the film two-dimensional; that is, one molecule deep. When the sorption region was not full, that is at lower relative humidities, portions of it would be filled with "islands" of liquid one molecule deep. However, he recognized ⁴ that at very low pressures the Langmuir conception of monomolecular sorption would be a closer approximation to the truth.

EXPERIMENTAL DISPROOF OF THE COMPRESSED FILM HYPOTHESIS FOR THE CASE OF HIGHLY POROUS BODIES SUCH AS CHARCOAL.

McBain and Britton ⁵ appear to have found an experimental disproof of the validity of the compressed film hypothesis, even in the latest form given by Polányi, for the case of highly porous bodies such as charcoal. They measured the sorption of nitrogen by active charcoal at pressures of 1 and 60 atmospheres, using the sorption balance. Whether or not the observations are corrected for the effect of buoyancy on the charcoal and its container, the sorption of nitrogen is greatly increased by increasing the pressure from 1 to 60 atmospheres. It is now readily shown that this is incompatible with the

¹ A. Eucken, *Z. Elektrochem.*, 1922, **28**, 11.

² A. Eucken, *Z. Elektrochem.*, 1922, **28**, 6, 257.

³ F. Goldmann and M. Polányi, *Z. physik. Chem.*, 1928, **132**, 321; M. Polányi and K. Welke, *Z. physik. Chem.*, 1928, **132**, 371.

⁴ F. Goldmann and M. Polányi, *Z. physik. Chem.*, 1928, **132**, 355.

⁵ J. W. McBain and G. T. Britton, *J. Am. Chem. Soc.*, 1930, **52**, 2198.

requirements of the compressed film theory, as will be demonstrated by the numbers in table 57.

The essential point is that the method of measurement exactly corresponds to the definition of sorption in that the increased weight observed is the excess of nitrogen present in the sorption region above the uniform concentration that exists in the surrounding atmosphere. The excess is supposed to be due to the extra compression existing within the sorption region. Now the behaviour of nitrogen under compression is well known, and in table 57 comparison is made between the increased weight in a given volume under a definite extra compression over that of an equal volume of the surrounding atmosphere. Take, for example, as a first assumption that the average extra compression within the sorption region is 1,000 atmospheres, then if the surrounding atmosphere is at 1 atmosphere, the sorption region will be under 1,001 atmospheres and the excess of nitrogen per cubic centimetre of sorption region will be 0.5849 gm. Similarly, if the surrounding gas is at 60 atmospheres pressure, that within the sorption region will be at 1,060 atmospheres and the excess of nitrogen per cubic centimetre of sorption region will now be 0.5279 gm. In other words, the sorption must decrease from 0.5849 to 0.5279 gm. on raising the atmospheric pressure from 1 to 60 atmospheres of nitrogen. Actually however, the experiments of McBain and Britton, in agreement with the less extensive and exact experiments of earlier workers, show that instead of falling off, the sorption is very greatly increased. Hence the nitrogen in the sorption region does not differ from that in the surrounding atmosphere by being under an extra compression of 1,000 atmospheres. The further similar comparisons in table 57 show that this is equally true of a compression of 100 atmospheres, 10 atmospheres or even the absurdly low value of 1 atmosphere of sorption compression.

This disproof of any compressed film hypothesis applies with certainty to active charcoal but ought to be supplemented by a similar experiment with, say, nitrogen and crystals of sodium chloride, in order to complete the disproof for plane

TABLE 57

Calculation, from Amagat's Data, of the Excess Concentration or Density of Nitrogen at 16° which would obtain at 1 atmosphere as compared with 60 atmospheres if Nitrogen in the Sorption Region is under any stated Extra Compressive Force, F atmospheres. The Density of Nitrogen at 1 atmosphere is 0.00118 and at 60 atmospheres is 0.07163*

F atms.	Density at 1 + F	Excess over density at 1 atms.	Density at 60 + F	Excess over density at 60 atms.	Remarks
1,000	0.5861	0.5849	0.5995	0.5279	Decrease †
100	0.1199	0.1187	0.1849	0.1133	Decrease †
10	0.0130	0.01182	0.08353	0.01190	} Very slight increase †
5	0.0071	0.00592	0.07759	0.00596	
1	0.0023	0.00112	0.0729	0.00127	

* E. H. Amagat, *International Critical Tables*, 1928, **3**, 17.

† Experiment, on the contrary, shows a many fold increase.

surfaces and non-porous bodies. Coolidge,¹ in a critical discussion of the various explanations of sorption, introduced the suggestion that the cavities in charcoal are not of sufficient magnitude to include a potentially thick adsorbed layer.

DISCREPANCIES IN THE COMPRESSED FILM HYPOTHESIS

The untruth even of Polányi's latest hypothesis of the compressed monomolecular film obeying the equation of state arises presumably from the tacit assumption therein involved that all places on a surface are indifferently alike so that further pressure merely squeezes the molecules more closely together. This neglects the molecular constitution of matter, which necessitates localized forces on the surface, centering round the individual molecules of the surface, which cannot be regarded as continuous. Short range forces must, therefore, be at a maximum in the neighbourhood of points on the surface, and attempts to slide the molecules closer together or further apart by continuous gradations, irrespective of the pattern of the surface, will therefore meet with a resistance that is foreign to the equation of state. The influence of cohesive forces such as are represented by a of van der Waals' equation is taken into account in all the different sorption hypotheses, as will appear in the sequel.

¹ A. S. Coolidge, *J. Am. Chem. Soc.*, 1926, **48**, 1795.

The properties of matter involved in sorption are very general. They are exhibited, in respect to heat effects, equally well in various types of sorption as in distinctively chemical reactions, as was demonstrated in Chapter XIV. This again is true of the volume changes (see table 58), which are known to accompany the same chemical reactions, similar to those which have been predicated with less certainty in cases of sorption. In both cases we have to deal with modes of close packing of atoms and molecules of finite size. The data in table 58 demonstrate that close union may involve such close packing of the separate constituents that, for example, when liquid water is added to a crystal with which it combines to form another crystalline compound, the increase in volume is less than that of the liquid water added.

In table 58 V_1 is the volume in cubic centimetres occupied by hydrate containing 1 gm. of water and V_2 is the volume in cubic centimetres occupied by the same salt anhydrous. The values in column 6 are the atmospheres required to compress 1 gm. of water to the respective volumes in column 5.

TABLE 58

Increase in Volume of a Salt upon addition of 1 gm. of Water when the Water has combined to form a Hydrate

Salt	Hydrate	V_1 in c.c.	V_2 in c.c.	$V_1 - V_2$.	Atms.
CuSO ₄	CuSO ₄ ·5H ₂ O	1.218	0.504	0.71	(19,000)
Al ₂ (SO ₄) ₃	Al ₂ (SO ₄) ₃ ·18H ₂ O	1.338	0.431	0.91	3,000
BaCl ₂	BaCl ₂ ·2H ₂ O	2.190	1.499	0.69	(22,000)
BaBr ₂	BaBr ₂ ·2H ₂ O	2.401	1.725	0.68	(25,000)
CdSO ₄	3CdSO ₄ ·8H ₂ O	1.728	0.925	0.80	10,000
CaSO ₄	CaSO ₄ ·2H ₂ O	2.059	1.272	0.79	(11,000)
Na ₂ CO ₃	Na ₂ CO ₃ ·10H ₂ O	1.089	0.237	0.85	6,000
MnSO ₄	MnSO ₄ ·4H ₂ O	1.469	0.709	0.76	(13,000)
FeCl ₂	FeCl ₂ ·4H ₂ O	1.433	0.696	0.74	(14,000)
CaO	Ca(OH) ₂	1.979	0.988	0.99	250
SO ₃	H ₂ SO ₄	2.945	2.242	0.70	(20,000)
H ₂ SO ₄	H ₂ SO ₄ ·H ₂ O	3.591	2.938	0.65	(35,000)
P ₂ O ₅	2H ₃ PO ₄	1.926	1.101	0.83	7,500
C ₄ H ₆ O ₃	2C ₂ H ₄ O ₂	6.352	5.235	1.12	Negative
(C ₂ H ₅) ₂ O	2C ₂ H ₆ O	6.476	5.763	0.71	(19,000)

Data such as are given in table 58 would, if they referred to sorption, be calculated in terms of the compressed film

theory as being due to the compressions shown in the last column. The fact that they give similar results to those derived from sorption data, as is seen from a comparison with values adduced in the second paragraph of this chapter (page 447), deprives this argument of its validity for highly compressed films.

Pearce and Johnstone¹ reveal a further discrepancy in the argument for thick compressed films from heats of sorption, where the excess over heat of condensation to ordinary liquid is ascribed to heat of compression.

“According to the Polányi theory, however, the surface of the adsorbed layer increases in distance from the surface of the adsorbent as more and more material is added, and finally it reaches the edge of the adsorption space. The adsorption potential, and thus the compressive forces, decrease very rapidly near the edge of the adsorption space. Hence the heat of compression must also decrease rapidly. In this range the heat of adsorption should decrease rapidly with the concentration until it finally equals the heat of vaporization.”

Although they have not tested this relation, and incline in general towards the thick compressed film theory, it may be pointed out that heats of sorption so far as is known do not in general fall off in the manner predicted.

¹ J. N. Pearce and H. F. Johnstone, *J. Phys. Chem.*, 1930, **34**, 1273.

CHAPTER XVIII

MONOMOLECULAR ADSORPTION

ADSORPTION THE RESULT OF THE TIME LAG BETWEEN CONDENSATION AND EVAPORATION OF MOLECULES STRIKING A SURFACE

A now familiar argument was developed by Kayser ¹ in 1881. He proceeded from the fact that solid bodies hold together, as proving the existence of cohesive forces, whether of a chemical or physical nature. In the case of a molecule in the interior of a solid these operate on all sides, but for molecules on the surface one side is free. Hence these exposed molecules must be able to hold to themselves molecules of a liquid or gas and form a monomolecular layer upon the surface. This layer may hold another layer less firmly or completely, and so on. Such sorption is favoured by pressure, but the forces operative are opposed by thermal vibration and hence sorption will diminish with rising temperature.

This idea was suggested briefly and less explicitly by Haber ² at a meeting of the Bunsen Gesellschaft in 1914. However, it is to Langmuir that we owe the fundamental advance in the subject of adsorption which was occasioned by his logical and decisive quantitative formulation of the factors involved in this train of thought.

Langmuir's development ³ of these ideas is distinguished for the clarity and precision of its formulation without any

¹ H. Kayser, *Wied. Ann. der Physik*, 1881, **14**, 463.

² F. Haber, *Z. Elektrochem.*, 1914, **20**, 521; *J. Soc. Chem. Ind.*, 1914, **33**, 50.

³ I. Langmuir, *J. Am. Chem. Soc.*, 1915, **37**, 1139; *Phys. Rev.*, (2), 1915, **6**, 79; 1916, **8**, 149; *Met. Chem. Eng.*, 1916, **15**, 468; *J. Am. Chem. Soc.*, 1916, **38**, 2221; 1917, **39**, 1848; *Proc. Nat. Acad. Sci.*, 1917, **3**, 141; *J. Am. Chem. Soc.*, 1918, **40**, 1361.

loss in generality. Furthermore, he has especially emphasized that intramolecular forces, whether chemical or physical, become relatively insignificant at distances greater than the few Ångstrom units that constitute the nearest approach of atomic centres.

Langmuir opens his discussion with the consideration that, in general, molecules and atoms of a gas striking a surface adhere to it for a longer or shorter time.¹ In other words, they do not undergo elastic reflection but are held upon the surface. At some subsequent time, such a molecule may evaporate from the surface.

"The length of time that elapses between the condensation of a molecule and its subsequent evaporation depends upon the intensity of the surface forces. Adsorption is the direct result of this time lag. If the surface forces are relatively intense, evaporation will take place at only a negligible rate, so that the surface of the solid becomes completely covered with a layer of molecules. In cases of true adsorption this layer will usually

¹ B. Baule, *Ann. der Physik*, (4), 1914, **44**, 145; H. Hertz, *Wied. Ann. der Physik*, 1882, **17**, 177. For a general discussion of relevant problems, see L. B. Loeb, *Kinetic Theory of Gases*, McGraw-Hill Book Co., Inc., New York, 1927. See also for detailed discussion and many illustrations, I. Langmuir, *Phys. Rev.*, (2), 1916, **8**, 149. For studies of the proportions of inelastic and elastic collisions with the molecules of gases upon a solid surface, see I. Langmuir, *J. Am. Chem. Soc.*, 1916, **38**, 2259; *Phys. Rev.*, (2), 1916, **8**, 149; *Z. Elektrochem.*, 1920, **26**, 197; R. Marcelin, *Compt. rend.*, 1914, **158**, 1419, 1674; *Ann. physique*, 1915, **3**, 185; M. Knudsen, *Ann. der Physik*, (4), 1915, **47**, 697; 1915, **48**, 1113; 1916, **50**, 472; K. Bennewitz, *Ann. der Physik*, (4), 1919, **59**, 193; R. Gross and M. Volmer, *Z. Physik*, 1921, **5**, 188; M. Volmer and J. Estermann, *Z. Physik*, 1921, **7**, 1, 13; R. W. Wood, *Phil. Mag.*, (6), 1915, **30**, 300; 1916, **32**, 364; J. Chariton and N. Semenov, *Z. Physik*, 1924, **25**, 287; J. K. Roberts, *Proc. Roy. Soc. (London)*, A, 1930, **129**, 146; M. C. Johnson, *Proc. Roy. Soc. (London)*, A, 1930, **128**, 432, 444; A. E. Martin, *Phil. Mag.*, (7), 1930, **9**, 97. Many of those investigated, particularly for chemically indifferent pairs such as noble gases or metals on glass, appear to differ greatly from the value $\alpha = 1$ for uniformly inelastic collisions with measurably extended life upon the surface. Langmuir has emphasized that the latter need not be of sufficient duration to produce temperature equilibrium between the gas molecule and the solid ("accommodation coefficient" = 1).

be not more than one molecule deep, for as soon as the surface becomes covered by a single layer the surface forces are chemically saturated. Where, on the other hand, the surface forces are weak the evaporation may occur so soon after condensation that only a small fraction of the surface becomes covered by a single layer of adsorbed molecules. In agreement with the chemical nature of the surface forces, the range of these forces has been found to be extremely small, of the order of 10^{-8} cm. That is, the effective range of the forces is usually much less than the diameter of the molecules. The molecules thus usually orient themselves in definite ways in the surface layer since they are held to the surface by forces acting between the surface and particular atoms or groups of atoms in the adsorbed molecule.”¹

“Molecules striking a surface already covered also condense, but usually evaporate much more rapidly than from the first layer. Hence, except when the vapour is nearly saturated, the amount of material adsorbed on a *plane surface* rarely exceeds that contained in a layer one atom (or molecule) deep.”²

“In some cases the rate of evaporation is so low that evaporation practically never occurs. This is what happens, for example, when a catalyst is poisoned by sulphur or arsenic compounds. In other cases, the rate of evaporation may be so high that the time that elapses between condensation and evaporation may be of the order of 10^{-12} seconds or even less.”³

Langmuir emphasizes the short-range character of interatomic and intermolecular forces. They are regarded as falling off with a high power of the distance. He estimates that for molecules of widely differing type these forces fall off to half value when one compares the force at the surface of an atom with that only $0.3 \text{ \AA}$. outside the surface. “Our present conception of the structure of atoms and molecules makes it impossible for us to conceive of any appreciable force which one atom or molecule can exert directly on others at distances greater than two or three Ångstrom units (10^{-8} cm.).”⁴

¹ I. Langmuir, *J. Am. Chem. Soc.*, 1918, **40**, 1362.

² I. Langmuir, *Phys. Rev.*, (2), 1915, **6**, 79.

³ I. Langmuir, *Trans. Farad. Soc.*, 1921, **17**, 9.

⁴ I. Langmuir, *Trans. Farad. Soc.*, 1921, **17**, 4. Compare the forces of very long range, up to 10^{-4} cm., believed in by all the older physicists, and the recent experiments of W. B. Hardy (see Chapter X, page 350).

LANGMUIR'S QUANTITATIVE FORMULATION

Langmuir's conception of monomolecular adsorption is found upon examination to be very elastic and to embrace many different types due to any kind of force, "chemical" or "physical", and to many different arrangements of the surface atoms both as to their configuration and their exposed attractive forces. It is perhaps simplest first to describe case (1) of the six which Langmuir explicitly distinguishes; namely, simple adsorption upon a homogeneous crystal surface exhibiting only one kind of "elementary space", or rather area. Each such area is assumed to be capable of holding only one molecule, whether by chemical or physical adsorption.

The rate at which molecules from a gas come into contact with an exposed surface is given by the equation for the rate of effusion of gases through small openings

$$m = p \cdot \sqrt{\frac{M}{2\pi RT}}.$$

"Here m is the number of grams of gas striking the surface per sq. cm. per second, M is the molecular weight, T the absolute temperature, p the pressure in bars, and R the gas constant 83.2×10^6 ergs per degree. If we let μ represent the number of gram molecules of gas striking each sq. cm. per second, then $\mu = m/M$, whence"¹

$$\mu = \frac{p}{\sqrt{2\pi MRT}} = 43.75 \times 10^{-6} \frac{p}{\sqrt{MT}}.$$

Nearly all these molecules will strike inelastically. The rate at which gas condenses on a bare surface will thus be $a\mu$, where a is close to unity. If θ is the fraction of the surface which is bare, the rate of condensation becomes $a\theta\mu$, because molecules striking an already occupied elementary space will either be elastically reflected or evaporate so quickly as to give the same effect. Similarly, the rate of evaporation may be set equal to v_1 for a completely covered surface and $v_1\theta_1$ for the fraction of the surface actually covered. For

¹ I. Langmuir, *J. Am. Chem. Soc.*, 1918, **40**, 1368.

equilibrium the rate of evaporation must equal the rate of condensation.

$$a\theta\mu = v_1\theta_1$$

Furthermore,

$$\theta + \theta_1 = 1$$

whence

$$\theta_1 = \frac{a\mu}{v_1 + a\mu}$$

If we set $a/v_1 = \sigma_1$ this becomes

$$\theta_1 = \frac{\sigma_1\mu}{1 + \sigma_1\mu}.$$

If η be the number of gram molecules of gas adsorbed per unit area of surface, then η is given by

$$\frac{N}{N_0}\eta = \theta_1 = \frac{\sigma_1\mu}{1 + \sigma_1\mu}$$

where N_0 is the number of elementary spaces per square centimetre of surface and N is the Avogadro number, 60.6×10^{22} molecules in any gram molecule.

Since μ is proportional to the pressure p , the above equation is equivalent to the expression

$$\frac{x}{m} = \frac{abp}{1 + ap}$$

where a and b are constants (see Chapter II, page 31). For example, b is proportional to N_0/N , the ratio of the number of molecules adsorbed per square centimetre when the surface is saturated to the Avogadro number. The other constant a is proportional to N/N_0 and to $\tau/\sqrt{2\pi MRT}$.

Langmuir designates the quantity σ_1 the "relative life," which he relates to the average life of a molecule adsorbed upon the surface. He distinguishes the average life of all the molecules which condense upon the surface N/N_{v_1} from the average life τ of all the molecules which strike the surface aN_0/N_{v_1} or $N_0\sigma_1/N$ whence

$$\eta = \frac{\tau\mu}{1 + \sigma_1\mu}.$$

At sufficiently low pressures, where this denominator approaches unity, $\eta = \tau\mu$ or $x/m = abp$, and hence the adsorption has a high negative temperature coefficient since τ is inversely proportional to the rate of evaporation ν_1 .

On the other hand, at high pressures where $\sigma_1\mu$ becomes large in comparison to unity, the amount adsorbed η approaches asymptotically a "saturation" value

$$\eta_{\infty} = \frac{\tau}{\sigma_1} = \frac{N_0}{N}$$

where every elementary space contains one adsorbed molecule. "At these higher pressures the amount adsorbed does not vary with the temperature except in so far as N_0 is dependent on temperature."¹ We shall return to a consideration of the significance of the constants of the Langmuir equation.

Langmuir proceeds to point out that if there are several kinds of elementary spaces, equations similar to the above can be set up for each kind, and the total adsorption will simply be their sum. If they are very different, the adsorption curve, although continuous, will tend to consist of steps.² With glass or charcoal he considers that the surface may be made up of an indefinitely large number of very different elementary spaces. The case where adjacent molecules can influence each other is also discussed by choosing elementary spaces large enough to adsorb more than one molecule.

Langmuir especially discusses the cases of adsorption where the molecules are adsorbed as atoms, because "the forces which hold adsorbed substances act primarily on the individual atoms rather than on the molecules". Each atom may occupy an elementary space, its rate of evaporation being

¹ I. Langmuir, *J. Am. Chem. Soc.*, 1918, **40**, 1370.

² This is presumably what A. J. Allmand and L. J. Burrage (*Proc. Roy. Soc. (London)*, A, 1931, **130**, 610) have in mind when they maintain that "the adsorption of vapours by charcoal is an essentially discontinuous process, and that, for example, an ordinary adsorption isothermal is composed of a series of loops, cutting one another at more or less well-defined pressures." Langmuir himself (*J. Am. Chem. Soc.*, 1918, **40**, 1389) found it necessary to assume that the sorption of carbon monoxide and of methane by glass (in the presence of mercury) took place in two stages, the first being completed at very low pressures.

negligibly small except when adjacent atoms combine and thus nearly saturate each other and leave the surface in pairs. When the atoms of two molecules occupy adjacent spaces, the pair of atoms evaporating may not be those originally paired in one molecule, so that isolated atoms are left on the surface.

" Let θ_1 be the fraction of the surface covered by adsorbed atoms, while θ is the fraction which is bare. In order that a given molecule approaching the surface may condense (and be retained for an appreciable time) on the surface, two particular elementary spaces must be vacant. The chance of one of these spaces being vacant is θ ; that both shall be vacant is θ^2 . The rate of condensation is thus equal to $a\theta^2\mu$. Evaporation only occurs when adsorbed atoms are in adjacent spaces. The chance that an atom shall be in a given space is θ_1 . Therefore, the chance that atoms shall be in adjacent spaces is proportional to θ_1^2 . The rate of evaporation of molecules from the surface is therefore equal to $v_1\theta_1^2$, where, as before, v_1 is the rate of evaporation from a completely covered surface. For equilibrium we then have the condition

$$a\theta^2\mu = v_1\theta_1^2$$

The number of gram molecules η of oxygen (O_2) adsorbed per unit area is given by

$$\frac{2N\eta}{N_0} = \theta_1.$$

" By combining these two equations with $\theta + \theta_1 = 1$, we may express η in terms of μ by means of a quadratic equation. Of most practical interest, however, is the case where the total amount of adsorption is only sufficient to cover a small fraction of the surface. We can, therefore, place approximately $\theta = 1$ and obtain

$$\frac{2N\eta}{N_0} = \sqrt{\sigma\mu}$$

where $\sigma = a/v_1$.

" Thus, in this case, even at relatively low pressures, the total amount of adsorbed gas varies in proportion to the square root of the pressure." ¹

Taylor has shown ² from ionization potentials and from heats of sorption that diatomic molecules of gases such as

¹ I. Langmuir, *J. Am. Chem. Soc.*, 1918, **40**, 1373.

² H. S. Taylor, *Proc. Roy. Soc. (London)*, A, 1926, **113**, 79.

hydrogen and nitrogen adsorbed on metals such as nickel and iron are retained in the form of adsorbed atoms.

GENERAL APPLICABILITY OF THE LANGMUIR THEORY

The essence of the Langmuir theory lies in the postulate that at least one atom of each adsorbed molecule is in direct contact with one or more atoms of the solid. Langmuir's formulation of adsorption as resulting from the time lag between condensation and evaporation and his emphasis on the inelastic nature of nearly all collisions of a gaseous molecule with a surface stresses this as the primary process of adsorption and therefore presupposes that activation is not required for primary adsorption.¹ What happens thereafter is quite a different matter. The adsorbed molecule or atom may evaporate, or it may proceed to diffuse into the solid, or it may combine with adjacent adsorbed atoms, it may combine with underlying atoms or may combine with other atoms or molecules striking the surface. Some of these processes will have a high temperature coefficient and may therefore be interpreted as requiring activation,² which appears to be the essential part of the viewpoint of Taylor.¹ Even diffusion into a space lattice may require "activation", especially when the lattice has to be locally expanded (compare Chapter IX, page 302).

Polányi³ pointed out in 1929 that according to London's calculations for homopolar bonds, comprised of coupled spinning electrons, no heat of activation is required for an exothermic reaction in which free atoms combine or are separated, and that the heat of activation in the endothermic

¹ Compare the apparently contrary mode of expression of H. S. Taylor, *J. Am. Chem. Soc.*, 1931, **53**, 578; H. S. Taylor and A. T. Williamson, *J. Am. Chem. Soc.*, 1931, **53**, 813; H. S. Taylor and A. Sherman, *J. Am. Chem. Soc.*, 1931, **53**, 1614.

² I. Langmuir (*J. Am. Chem. Soc.*, 1913, **35**, 122; 1916, **38**, 2254, footnote 1) pointed out that the equation for rate of evaporation "is substantially equivalent to Arrhenius' equation for the temperature coefficient of reaction velocity." Compare Chapter III, page 43.

³ M. Polányi, *Z. Elektrochem.*, 1929, **35**, 562; compare 1921, **27**, 142. For calculations of heats of activation, see H. Eyring and M. Polányi, *Naturwissenschaften*, 1930, **18**, 914.

direction of such reactions does not exceed the heat of reaction. For molecular interactions, a definite amount has to be added to both these heats of activation. This heat of activation will be required after adsorption for a rearrangement of the two adsorbed molecules ; but it will be less than for the same reaction in the gaseous phase on account of the strong tendency towards distortion or sometimes complete separation of the atoms of the adsorbed molecule.

The high heats of sorption of atoms as compared with the corresponding molecules upon metal surfaces is interpreted as showing true chemical combination with the surface atoms involving a strictly defined homopolar bond, reaffirming Langmuir's original view. Such surface compounds can exist at temperatures and pressures which are quite impossible for their nearest relations amongst pure chemical compounds. Hence the bonds with the surface require no more activation energy than other atomic reactions. It follows that when the valence forces are insufficient to separate the adsorbed molecule, only the balance of the activation energy has to be supplied for the reaction to proceed after primary adsorption of the molecules. Any strain applied to the molecule would have a similar influence. This strain will in general occur in cases described as multiple adsorption (see this chapter, page 488).

The mechanism of adsorption so definitely yet generally outlined by Langmuir has proven almost universally convincing in so far as distinctly chemical behaviour is concerned. One might go even further and reclaim for the subject of sorption some interactions that have been classified as purely chemical. For example, the combination of oxygen or carbon monoxide with hæmoglobin undoubtedly leads to union of four mols of the gas with definite local chemical groups in the 68,500 grams that constitute one mol of hæmoglobin, the remaining mass being indifferent.¹ Nevertheless, if the active

¹ See the criticism in *Nature*, 1923, **111**, of Wo. Ostwald's view that this is a case of sorption (also W. M. Bayliss, *Nature*, 1923, **111**, 666) by N. K. Adam, pp. 496, 844 ; A. V. Hill, p. 843 ; J. Barcroft, p. 844 ; W. E. L. Brown, p. 881.

groups are exposed upon a surface reacting with a gas, the mechanism described by Langmuir, supplemented in general by the mobility in adsorbed films demonstrated by Volmer,¹ must be involved in the process. In other words, chemical reaction upon a surface must conform to the laws of sorption.²

Many cases of sorption have been found empirically to be in accordance with the Langmuir formula $\frac{x}{m} = \frac{abp}{1 + ap}$. This is shown, for example, in the sorption of gases or vapours by drastically evacuated charcoal, as in figs. 142, 143 and 144, taken from the measurements of McBain and Britton,³ where the Langmuir formulation demands a straight line graph.

It is of special interest that the famous data of Titoff, Richardson and Miss Homfray, in particular for carbon dioxide and charcoal, which served as the basis of Berényi's original calculations in support of Polányi's restatement of the classical compressed film theory (Chapter XVII, page 450), agree even better with the Langmuir equation. This is demonstrated in Zeise's graphs given in figs. 145⁴ and 146⁵ which include also data for nitrogen and ammonia. Similar results are obtained from Richardson's data for ammonia, Titoff's for nitrogen and Miss Homfray's for argon.

¹ For example, the average life of a caesium atom on a tungsten filament at 387° C. is one second, but it may travel distances on the surface a million times its own diameter (J. A. Becker, *Phys. Rev.*, (2), 1927, **29**, 364).

² This view here suggested by the writer that the laws of sorption apply to all surface actions where no phase separates, invalidates the classical conclusion of J. M. van Bemmelen (*Die Absorption*, T. Steinkopff, Dresden, 1910) which showed, as he thought, that there exist no hydrates of such oxides as alumina, silica and ferric oxide, and re-interprets them more in conformity with ordinary chemical knowledge. It would also justify the discussion of base exchanges in zeolites as examples of sorption. D. I. Hitchcock (*J. Am. Chem. Soc.*, 1926, **48**, 2870) has pointed out the formal identity of Langmuir's formula with the mass law equation for the reversible equilibrium of a homogeneous reaction involving the dissociation of a binary compound.

³ J. W. McBain and G. T. Britton, *J. Am. Chem. Soc.*, 1930, **52**, 2217, 2218 and 2220, figs. 14, 15 and 16.

⁴ H. Zeise, *Z. physik. Chem.*, 1928, **136**, 409, figs. 6 and 7.

⁵ H. Zeise, *Z. physik. Chem.*, 1928, **136**, 408, figs. 3 and 4.

In examining the various hypotheses put forward to explain sorption, we found capillary condensation (Chapter XVI) to

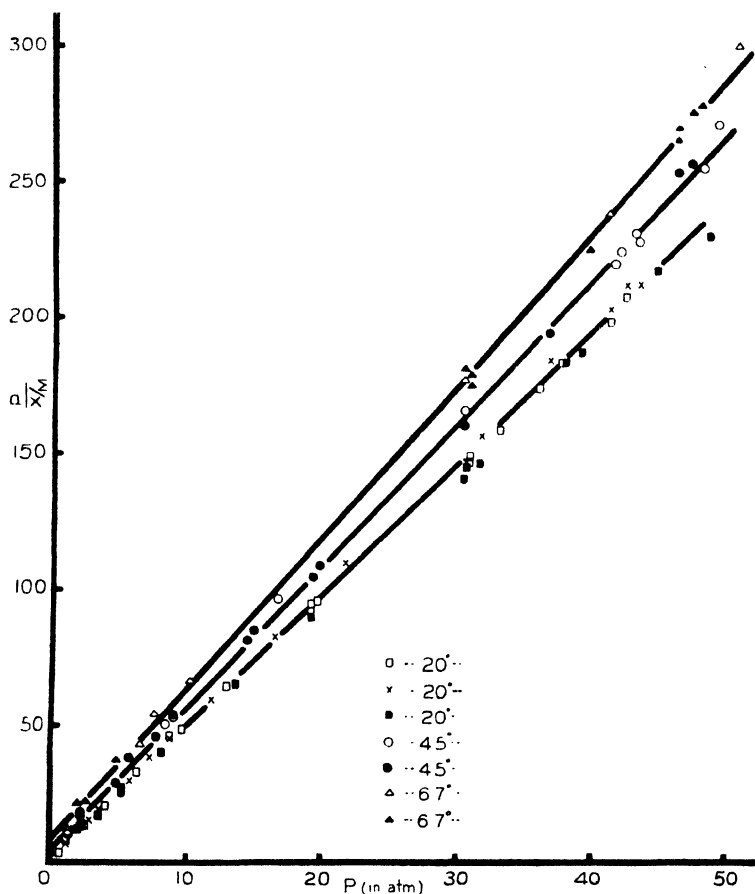


Fig. 142.—Comparison of the Isotherms observed with Nitrous Oxide and Activated Sugar Charcoals at various Temperatures with the Straight Lines demanded by the Langmuir Formula.

be a different and supernumerary phenomenon. The quantitative treatment either of this or of the conception of a film due to attraction of molecules towards the solid surface led

almost irresistibly to the conclusion that, in general, sorbed molecules are in direct contact with the atoms of the solid. Thus we come back to the monomolecular adsorbed layer

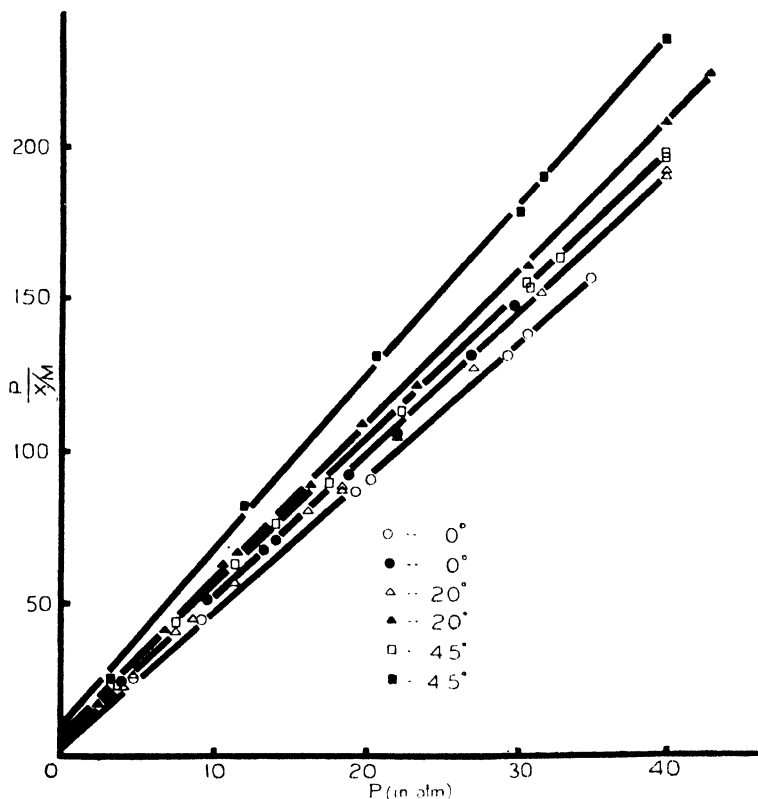


Fig. 143.—Comparison of the Isotherms observed with Ethylene and Activated Sugar Charcoals at various Temperatures with the Straight Lines demanded by the Langmuir Formula.

which Langmuir's chemical and physical arguments have done so much to explain. We see clearly that the most definitely chemical reaction, as long as it occurs at a surface, is conditioned by the laws of sorption just as is the most indifferently physical adhesion of a molecule to a surface.

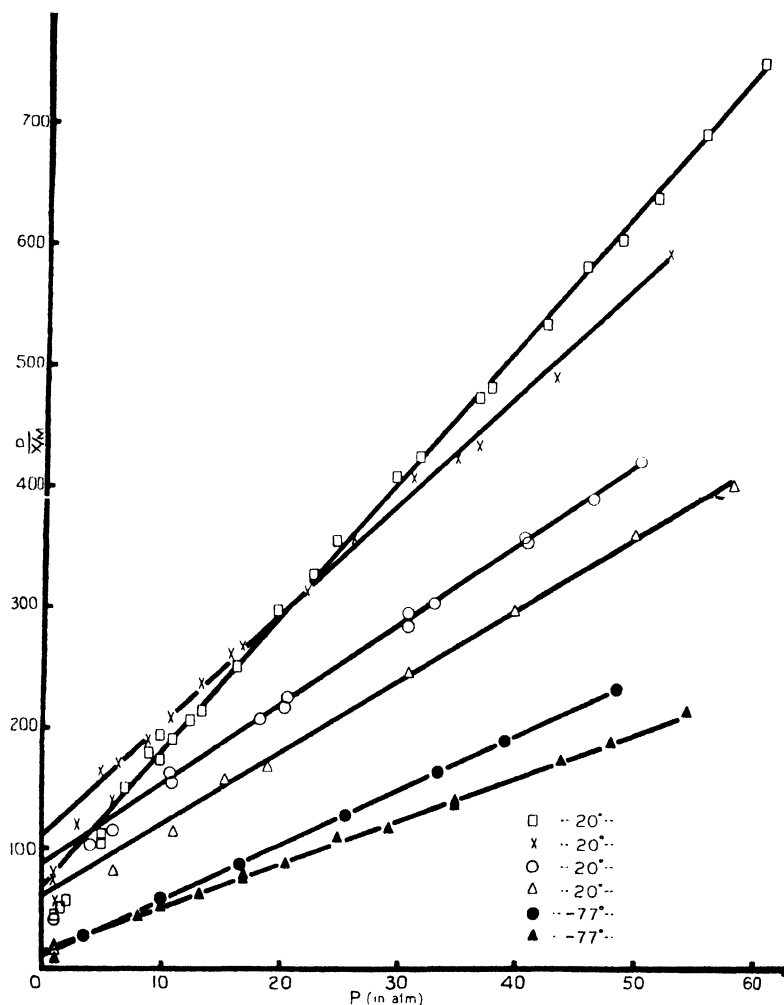


Fig. 144.—Comparison of the Isotherms observed with Nitrogen and Activated Sugar Charcoals at various Temperatures with the Straight Lines demanded by the Langmuir Formula.

$$x = \frac{c_1 c_2 p}{1 + c_2 p}$$

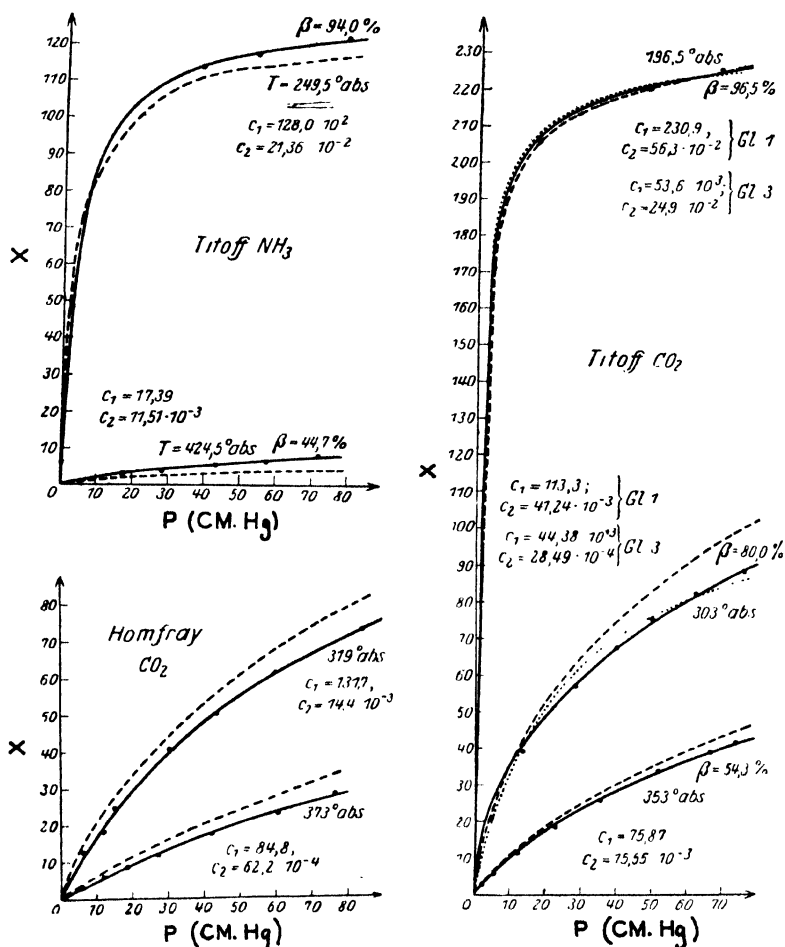


Fig. 145.—Comparison by Zeise of the Experimental Points for Observed Sorption with the Broken Curves of Berényi for the Polányi Theory and the Continuous Curves representing the Langmuir Monomolecular Formula. x is the Sorption in milligrams per gram of Charcoal; c_1 and c_2 are Arbitrary Constants.

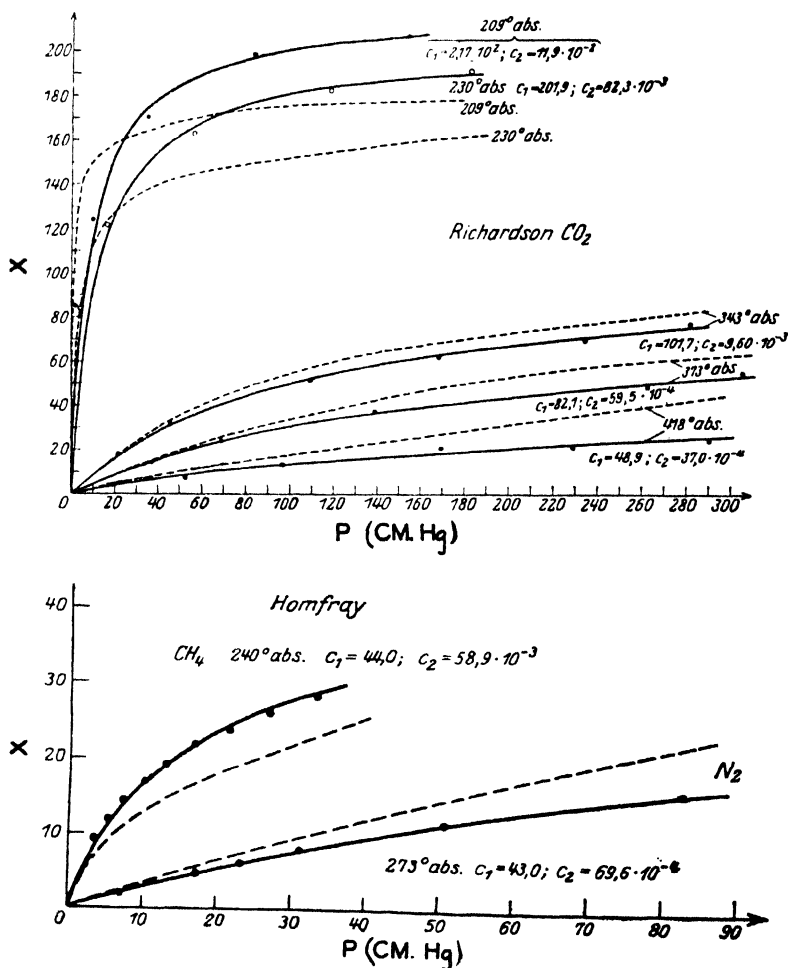


Fig. 146.—Comparison by Zeise of the Experimental Points for Observed Sorption with the Broken Curves of Berényi for the Polányi Theory and the Continuous Curves representing the Langmuir Monomolecular Formula. x is the Sorption in milligrams per gram of Charcoal; c_1 and c_2 are Arbitrary Constants.

Langmuir's ¹ experiments on electron emission from filaments of thoriated tungsten, shown ² to produce by diffusion from the interior a layer of thorium upon the surface not more than one atom deep and a monatomic layer of oxygen upon this, constitute excellent examples of purely physical and distinctively chemical phenomena in sorption.

The phenomena observed in connexion with the clean-up of oxygen by a tungsten filament ³ constituted a clear demonstration of the Langmuir theory, in this case to the exclusion of all others. Some of the salient facts may be summarized as follows :

(1) The sorption of oxygen upon tungsten is very stable. Thus the electron emission of tungsten at 1,600° C. is reduced several thousandfold by exposure to only one millionth of an atmosphere pressure of oxygen. No visible film is formed.

(2) At 3,000° C. 50 per cent of the oxygen molecules which strike a tungsten filament form the compound WO_3 which distils on to the glass. Consideration of the number of atoms in this compound shows that the surface of the tungsten must therefore be half covered with oxygen at 3,000° C.

(3) Hydrogen, when alone in a lamp, dissociates at 1,500° C. into atoms ; these adhere to the glass or reduce any of the oxide WO_3 with which they come into contact upon the glass. Hence the pressure upon the hydrogen rapidly decreases. This process is completely stopped by a trace of oxygen until all the oxygen has reacted to form a compound WO_3 . Then suddenly the hydrogen cleans up.

It is therefore seen that oxygen adsorbed on tungsten is incapable of reacting with hydrogen at 1,500° C. It therefore differs wholly from the highly compressed oxygen postulated by the classical film theory. Nor, again, is it like the compound WO_3 ; nor can it be more than one layer deep.

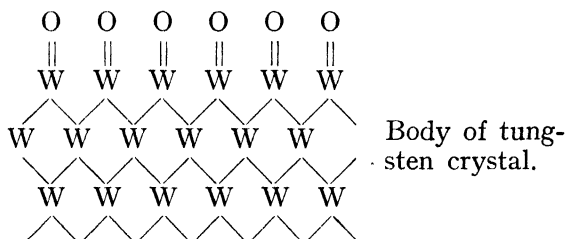
All this is pictured diagrammatically in the following hypo-

¹ I. Langmuir, *Phys. Rev.*, (2), 1914, **4**, 544 ; 1922, **20**, 107 ; 1923, **22**, 357.

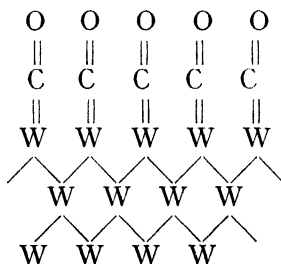
² I. Langmuir, *J. Am. Chem. Soc.*, 1916, **38**, 2281.

³ I. Langmuir, *J. Am. Chem. Soc.*, 1913, **35**, 105 ; 1915, **37**, 1148 ; 1916, **38**, 2271.

thetical cross sections through a crystal of tungsten and its surface. The oxygen is held to the tungsten by both primary valencies of each atom and is chemically saturated. This, however, does not constitute an oxide of tungsten by itself, for the tungsten atoms in turn form a continuation of the space lattice of the crystal beneath.



Similarly, a diagram for a monomolecular layer of carbon monoxide upon tungsten must represent it as being attached by two of the primary valencies of carbon.



Langmuir ¹ found that certain oxygen was completely removed from graphite only when heated for nearly half an hour at 2,000° C. in the highest vacuum. This he represented by a diagram exactly like that for the oxygen on tungsten. Shilov, Shatunovska and Chmutov ² distinguish three other modes of chemical attachment of oxygen to carbon in active charcoal, depending upon its previous treatment. In one, each atom of oxygen is held to two separate carbon atoms

¹ I. Langmuir, *J. Am. Chem. Soc.*, 1916, **38**, 2276.

² N. Shilov, H. Shatunovska and K. Chmutov, *Z. physik. Chem. Abt. A*, 1930, **149**, 211.

and these in turn to other carbon atoms ; in the second, each oxygen atom is similarly held but each surface carbon atom is linked to two separate oxygen atoms ; in the third, the surface carbon atoms are arranged in groups of two with three oxygen atoms, one of which links the two carbon atoms.

There is a tendency for certain writers to exclude any chemical phenomena from the subject of adsorption. This appears to the writer as much unjustified as it is to exclude from the concept of chemical combination any compound except cases of shared and symmetrically coupled electrons. Many kinds and degrees of chemical combination have always been recognized by chemists and many have not yet been either classified or explained in terms of current theory.¹ Langmuir has obscured the issue by postulating that all forces, such as those of van der Waals or surface tension, acting between atoms or molecules are all to be called chemical. Some, like Ruff,² accept the Langmuir theory for certain portions of a charcoal surface whilst retaining the classical compressed theory for other parts. Palmer,³ in utilizing Langmuir's theory to explain the phenomena of coherers in various atmospheres, finds the sorption to comprise primary physical adsorption, solid solution, and several varieties of chemical adsorption, the latter being distinguished by high heat of desorption. It is well known that sorption from solutions is often followed or accompanied by further chemical change ;⁴ this is sometimes termed chemisorption.⁵

¹ As an illustration, M. L. Huggins and J. Field, 2nd, *Science*, 1926, **63**, 454 ; compare Chapter XX.

² O. Ruff, *Ber.*, 1927, **60**, 426 ; *Kolloid-Z.*, 1926, **38**, 174.

³ W. G. Palmer, *Proc. Roy. Soc. (London)*, A, 1924, **106**, 55 ; 1926, **110**, 133 ; 1929, **122**, 487.

⁴ For example, see J. M. van Bemmelen, *Die Absorption*, p. 405 (Steinkopff, Dresden, 1910) ; W. M. Bayliss, *Proc. Roy. Soc. (London)*, B, 1911, **84**, 81 ; H. N. Gilbert, *J. Phys. Chem.*, 1914, **18**, 586 ; E. Wedekind and H. Rheinboldt, *Ber.*, 1914, **47**, 2142 ; 1919, **52**, 1019 ; E. Wedekind and H. Wilke, *Kolloid-Z.*, 1914, **34**, 83, 283 ; 1924, **35**, 23 ; E. Wedekind, *Z. angew. Chem.*, 1926, **39**, 738.

⁵ The term is due to H. von Euler and his pupils ; see for example, V. Morávek, *Arkiv Kemi Mineral. Geol.*, 1923, **8**, No. 30.

Seldom indeed will a case of pure physical adsorption upon a plane surface be realized. It is abundantly evident from the review of the experimental observations in previous chapters that nearly all surfaces are porous, corroded and chemically active and that some omnibus designation such as sorption is needed to embrace the manifold phenomena in this field of heterogeneous interaction and equilibria.

SIGNIFICANCE OF LANGMUIR TERMS IN RELATION TO OTHER QUANTITIES

On the basis of statistical considerations similar to those used by O. Stern in deriving his vapour pressure formula, Sexl¹ derived an equation which agrees completely with that of Langmuir. It showed that the fraction of the molecules adsorbed on a square centimetre that evaporate per second is $\nu e^{-\frac{\chi}{kT}}$, where ν is the vibration period of the adsorbed molecule and χ is the work required to remove it into the gas phase. The area of surface required to hold one molecule was not as satisfactorily ascertained.

Frenkel² follows the same train of thought as Langmuir and arrives at the same result as Langmuir and that just quoted for Sexl. In addition, combining the ideas of Langmuir and Knudsen for gases in which the mutual attraction of the sorbed molecules is greater than their attraction by the solid, he defines the critical temperature of reflection below which the adsorbed atoms will aggregate, at first to form doublets and then larger masses. Langmuir had emphasized that this temperature must likewise depend upon the pressure which governs the rate at which molecules strike

¹ T. Sexl, *Z. Physik*, 1928, **48**, 607.

² J. Frenkel, *Z. Physik*, 1924, **26**, 117. As shown by F. J. Wilkins and A. F. H. Ward (*Nature*, 1929, **124**, 482), Frenkel made a mistake in recording his final equation. The right-hand side of the bracket should be placed outside the equation so as to include within it the exponential term; namely,

$$\frac{S}{n} = \sigma_0 \left(1 + \frac{\sqrt{2\pi m k T}}{p \sigma_0 \tau_0} \cdot e^{-\frac{u_0}{kT}} \right).$$

the surface. Chariton and Semenoff ¹ found that this was the case. For each pressure there is a critical temperature. For each temperature there is a critical pressure below which the formation of close packed, two-dimensional phases or patches upon the surface does not occur.

Hückel ² deduces from the Maxwell-Boltzmann distribution law ³ for sorbed molecules far apart, each held by only one elementary space, only very short range forces being involved, for the number of mols sorbed per square centimetre

$$x = \frac{\mathcal{J} z v e^{\frac{\phi}{RT}}}{1 + v e^{\frac{\phi}{RT}}}$$

an equation of the Langmuir form, where $\mathcal{J}$ is the density of the gas, z is the number of elementary spaces per square centimetre divided by the Avogadro number N , v is the volume of N adsorption spaces, so that zv is the total volume of the elementary spaces per square centimetre, and ϕ is the adsorption potential per mol. If his equation is identified with that of Langmuir, the average life ν_1 of an adsorbed

molecule becomes equal to $e^{\frac{\phi}{RT}} \cdot \frac{v}{N} \cdot \sqrt{\frac{2\pi M}{RT}}$ which yields the

¹ J. Chariton and N. Semenoff, *Z. Physik*, 1924, **25**, 287; N. Semenoff, *Z. physik. Chem.*, Abt. B, 1930, **7**, 473; J. Estermann, *Z. Elektrochem.*, 1925, **31**, 441.

² E. Hückel, *Adsorption und Kapillarkondensation*, p. 159 (Akademische Verlagsgesellschaft, m.b.H., Leipzig, 1928). He criticizes the divergent result obtained by E. Jaquet ("Theorie der Adsorption von Gasen," *Fortschritte Chem., Physik, physik. Chem.*, Series B, 1925, **18**, Heft 7, p. 55) and also by B. Iliin (*Z. physik. Chem.*, 1923, **107**, 145) from the same premises.

³ Many writers avail themselves of the approximate application of the distribution law by placing the ratio of the number of molecules in one cubic centimetre of gas N_1 to the number of adsorbed molecules N_a contained in a sorption volume δ cm. deep upon 1 sq. cm. of surface

$$\frac{N_1}{N_a} = \delta e^{-\frac{Q}{RT}}$$

where Q is the heat of sorption per gram mol.

temperature coefficient. The Langmuir constant a here becomes

$$a = ve^{\frac{\phi}{RT}}.$$

Polányi¹ replaces the volume of action of the elementary space by the volume occupied by all possible vibrations of a single adsorbed molecule of period ν . Here a becomes

$$a = \left(\frac{\sqrt{\frac{2\pi kT}{m}}}{2\pi\nu} \right)^3 e^{\frac{\phi}{RT}}.$$

Jaquet² likewise deduces sorption isotherms, considering several suggestions for allowing for intermolecular action, and the equation which he found to agree best with the experiments is essentially the same as that of Langmuir. He also discusses a method for estimating the maximum adsorption energy from the observed temperature coefficient of the initial slopes of the isotherms, which several later writers have attempted to apply.³

Kar and Ganguli⁴ likewise develop the Langmuir formula by statistical methods. They obtain for the reciprocal of Langmuir's constant, a ,

$$\frac{1}{a} = \frac{\sqrt{2\pi MRT}}{hN} \cdot e^{-\frac{a}{RT}}$$

or, more generally,

$$\frac{1}{a} = \frac{\sqrt{2\pi MRT}}{\mathfrak{h}N} \cdot e^{-\frac{a}{RT}}$$

where $\mathfrak{h}$ becomes equal to Planck's constant h for unimolecular sorption and a is the absorption potential. They find good agreement with the usually adduced data of Titoff and Miss Homfray.

¹ M. Polányi, *Z. physik. Chem.*, Abt. A, 1928, **138**, 460.

² E. Jaquet, "Theorie der Adsorption von Gasen," *Fortschritte Chem., Physik, physik. Chem.*, Series B, 1925, **18**, Heft 7, pp. 9 and 34.

³ For example, H. Kälberer, H. Mark and C. Schuster, *Z. Elektrochem.*, 1929, **35**, 600.

⁴ S. C. Kar, *Physik. Z.*, 1925, **26**, 615; K. C. Kar and A. Ganguli, *Physik. Z.*, 1929, **30**, 918; A. Ganguli, *J. Phys. Chem.*, 1930, **34**, 665.

It may be of interest to note that the simple Langmuir expression deduced on page 468 (this chapter) corresponds to the first term of the expansion of Iliin's ¹ general formula for sorption, intended to embrace both absorption (solution) and monomolecular adsorption,

$$\frac{x}{m} = \frac{x_{\max}}{m} (1 - e^{-kp}).$$

Gorbatschew ² likewise deduces the Langmuir form of the equation, assuming short distance forces of attraction and utilizing the conception of lines of force that pass through each sorbed molecule, the number depending upon the amount of adsorption and being the same for each adsorbed molecule. He passes in review ³ various formulæ; Langmuir's and Reichstein's follow on the assumption that the number of lines leaving the surface is constant; Schmidt's and Williams' equations follow on the assumption that the number is inversely proportional to the concentration of the *unadsorbed* substance; "Freundlich's" (classical) and Kroecker's equations follow on the assumption that the number of lines of force leaving the surface is inversely proportional to the amount of substance sorbed.

The observations of Wulff and Luce ⁴ show how readily a slight alteration in surface, such as local curvature or imperfection, leads to the building up of thicker layers or even crystal nuclei in certain cases. Magnus ⁵ by a few typical calculations, assuming arbitrarily that the attractive force upon a molecule falls off with the sixth power of the distance from each element of the surface, shows that a molecule would be held in a hemispherical concavity of approximately

¹ B. Iliin, *Z. physik. Chem.*, 1923, **107**, 149.

² A. Gorbatschew, *Z. physik. Chem.*, 1925, **117**, 133 and 135.

³ A useful review of sorption formulæ with a bibliography of 117 references has been made by E. Swan and A. R. Urquhart, *J. Phys. Chem.*, 1927, **31**, 251.

⁴ J. Wulff, *Nature*, 1929, **123**, 682; *Naturwissenschaften*, 1929, **7**, 389; L. R. Luce, *Ann. physique*, (10), 1929, **11**, 167; see Chapter VII, page 237, and Chapter IX, page 307, for quotations.

⁵ A. Magnus, *Z. anorg. allgem. Chem.*, 1926, **155**, 221.

equal size three times more strongly than by a plane surface and that similar reasoning applies to crevices, pores or unevennesses of this order of magnitude. This is of importance in finely porous materials.

CHANGE OF MAXIMUM SORPTION WITH TEMPERATURE

The Langmuir hypothesis has been repeatedly criticized because the equation, whether as deduced by Langmuir, Volmer, Hückel, Frenkel or Gorbatschew, appears to postulate a saturation value independent of temperature. Experiment, on the other hand, distinctly indicates that the amount of a vapour which can be sorbed falls off with increase of temperature almost as fast as the liquid overflows from a vessel of constant volume when similarly heated; and that of a gas alters even more.

It is true that Langmuir in the sentence quoted on page 469 of this chapter made the verbal proviso that the number of elementary spaces might vary with temperature. However, various other suggestions have been made. The writer would suggest that the real effect is that pictured in the foregoing paragraph; namely, that close packed matter does expand with temperature. This must be particularly evident in all cases of persorption in finely porous bodies, but must be true wherever the elementary spaces are sufficiently close to each other or when the attractive force, in comparison to the size of the adsorbed molecule, is fairly uniformly distributed over the surface (compare the writer's remarks on steric hindrance, Chapter III, page 41).

Other suggestions include that of Zeise¹ that the accessibility of the finest pores changes with temperature, which corresponds to Langmuir's proviso. Alternatively, the mode of binding to the elementary spaces might vary with the nature of the gas and the temperature.

Hückel² has several suggestions: first, as to the main premises themselves; secondly, as to the assumptions that there is only one kind of elementary space and that each can

¹ H. Zeise, *Z. physik. Chem.*, 1928, **136**, 414.

² E. Hückel, *Adsorption und Kapillarkondensation*, 1928, p. 162.

hold only one molecule ; and thirdly, as to the neglect of the forces between the adsorbed molecules.

Experimentally, both of the Langmuir constants have to be chosen empirically and both vary with temperature, and not in the manner calculated by Polányi.

Langmuir, of course, did not intend his equation to apply to porous bodies, to which in fact it does apply if one chooses the necessary values of the constants a and b for each isotherm independently (compare figs. 142 to 146). Polányi points out that Zeise's value for the number of elementary spaces, if the Langmuir constant is to be so interpreted, appears to be halved for a rise of 100°C. and that the dependence of the other constant, b , upon the temperature is not exponential as would be expected from the formulations on pages 483 and 484 (this chapter). Zeise's reply ¹ with regard to the last statement is that the temperature effect is of the right order, being approximately in inverse proportion to the fifth power of the absolute temperature, and that anyway the formulæ are faulty through the use of classical instead of quantum mechanics. The temperature coefficient of saturation could be explained by thermal agitation rendering elementary spaces ineffective as well as by suggesting that adsorption does not correspond to the simplest case suggested by Langmuir but is followed or accompanied by some secondary effect, such as attachment to a second neighbouring elementary space or through the influence of induced dipole moments.

Wilkins and Ward ² also decide in favour of the Langmuir theory after taking into account the mobility of the adsorbed material upon the surface. They liken the temperature expansion of the two-dimensional sorption layer to that of a gas at constant pressure and find them of the same order of

¹ H. Zeise, *Z. Elektrochem.*, 1929, **35**, 428 ; *Z. physik. Chem.*, Abt. A, 1928, **138**, 289.

² F. J. Wilkins and A. F. H. Ward, *Z. physik. Chem.*, Abt. A, 1929, **144**, 259. They recall that reflection of electrons showed that a gas adsorbed on nickel at room temperature exhibits a definite spacing, but not when it is at a temperature of 150°C. (C. J. Davisson and L. H. Germer, *Phys. Rev.*, (2), 1927, **30**, 705 ; L. H. Germer, *Z. Physik*, 1929, **54**, 408).

magnitude. This is a more quantitative form of the writer's view, which, on the other hand, is more general.

More recently, Bradley,¹ proceeding from Zeise's empirical temperature coefficients and substituting them for the Langmuir constants a and b , derives an isotherm in good agreement with the usually cited data of Titoff and Richardson. To identify this with a virial equation in two dimensions, it is necessary to set

$$\log ab = -\frac{\Delta F_0}{RT} = \frac{k_1}{T} + k_2$$

where F is free energy and k_1 and k_2 are constants, k_1 being equal to $\Delta H_0/RT$ where ΔH_0 is the change in heat content.

This relation is in agreement with the data. Further, $\frac{1}{2a}$ has to be set equal to the term $B_0 - \frac{c}{T^3} - \frac{\Delta I_0}{RT^2}$ taken from the virial form of the equation of Beattie and Bridgeman.²

MULTIPLE ADSORPTION OF A MOLECULE ON MORE THAN ONE ATOM OF THE SOLID

The hypothesis of multiple adsorption as a special case has repeatedly found favour. To it belong the suggestions of Polányi and of Zeise (pages 471, 472 and 487) which follow the conception of Burk,³ 1926, described in the following quotation.

"The extremely short range of atomic forces limits the effectiveness of adsorptive forces to a region within an atomic diameter of the surface. Furthermore, the portions of this force region directly overlying the surface atoms would be the seat of forces enormously more intense than the regions in between these atoms. Such a structure of the adsorptive forces leads to the conception that the separate atoms of the adsorbed molecule are attached to the separate atoms of the surface. Insofar as the geometric arrangement of the relevant atoms does not permit this, the

¹ R. S. Bradley, *Phil. Mag.*, (7), 1931, **11**, 692.

² J. A. Beattie and O. C. Bridgeman, *J. Am. Chem. Soc.*, 1927, **49**, 1665; 1928, **50**, 3133.

³ R. E. Burk, *J. Phys. Chem.*, 1926, **30**, 1134.

adsorbed molecule will be stretched, an action which must play a part in catalysis."¹

Similar views were expressed by Adkins.² Balandin³ has shown that this conception is especially fruitful in the field of heterogeneous catalysis (see Chapter XIX).

Zeise⁴ found that the sorption of methane, nitrogen and oxygen on glass at -183°C. was equal to

$$q = \sqrt{\frac{k_1 k_2 p}{1 + k_2 p}}$$

where the right-hand side of the equation is the same as for Langmuir's simplest case except that it is taken to the power $1/2$. Zeise, following Langmuir's mode of reasoning but assuming that a molecule must be held simultaneously by two elementary spaces, deduces this equation, evaluating the constants in terms of the usual Langmuir factors ($q.v.$).

THE FORMULATION OF WILLIAMS AND HENRY

A formulation both of isosteres and isotherms has been deduced by Williams⁵ from a few of the fundamental relations of the kinetic theory. It has been criticized for the complexity or awkwardness of the argument, but it appears to the writer to be of especial interest because it explicitly includes the thickness of the sorbed layer without *a priori* assumptions and yet in a form which can be evaluated by comparison with experiment. Debye and Jaquet⁶ have made use of the same premises.

¹ R. E. Burk and D. C. Gillespie, *Proc. Nat. Acad. Sci.*, 1928, **14**, 470.

² H. Adkins and B. H. Nissen, *J. Am. Chem. Soc.*, 1923, **45**, 809; 1924, **46**, 130; H. Adkins and W. A. Lazier, *J. Am. Chem. Soc.*, 1924, **46**, 2291; F. Bischoff and H. Adkins, *J. Am. Chem. Soc.*, 1925, **47**, 807.

³ A. A. Balandin, *Z. physik. Chem., Abt. B*, 1929, **2**, 289.

⁴ H. Zeise, *Z. physik. Chem.*, 1928, **136**, 397.

⁵ A. M. Williams, *Proc. Roy. Soc. Edin.*, 1918, **38**, 23; 1919, **39**, 48; *Proc. Roy. Soc. (London)*, A, 1919, **96**, 287, 298. Like Eucken and Polányi, he does not allow for dependence of sorption potential or volume of the sorption space upon temperature.

⁶ E. Jaquet, *Fortschritte Chem., Physik, physik. Chem.*, Series B, 1925, **18**, Heft 7, p. 3; compare this chapter, page 483, footnote 2.

Williams' isotherm ¹ is identical in form with that deduced by Henry ² from wholly different assumptions, modelling his reasoning on that of Langmuir.

Williams defines the adsorption volume as the product of the surface area and the effective range of molecular attraction δ , which is also set equal to the thickness of the adsorbed layer. It is therefore assumed of uniform thickness, and the attractive forces are not regarded as significantly localized. When a gas, obeying the gas law $pV = RT$ or $p = cRT$, is adsorbed by an indefinitely large surface S , its change of energy E per mol is given by the reaction isochor

$$E = V \cdot \left\{ T \left(\frac{\partial p}{\partial T} \right)_x - p \right\}$$

where x is the amount in mols sorbed per unit of solid.

$$E = \frac{RT^2}{p} \cdot \frac{\delta p}{\delta T} - RT$$

or, in more familiar form,

$$E = RT^2 \cdot \left(\frac{\delta \log c}{\delta T} \right)_x \cdot \cdot \cdot \cdot \cdot \quad (1)$$

Comparing the change of energy upon passing from the gaseous volume into the adsorbed volume V_x ,

$$E = RT \log \frac{V}{V_x} = RT \log \frac{1}{cV_x}$$

If a molecule of diameter σ is adsorbed when its centre is within a distance δ from the surface and the closest approach of its centre to the surface is $\sigma/2$, we may substitute for V_x the volume $S(\delta - \sigma)/x$. Whence,

$$E = RT \log \frac{x}{cS(\delta - \sigma)} \cdot \cdot \cdot \cdot \cdot \quad (2)$$

Williams then finally assumes that the law of attraction of the solid for the molecules of the gas is proportional to the square root of the cohesive forces (van der Waals' a) both of solid and of gas, and is such that if μ is a general constant

¹ See Chapter II, page 31, fig. 15.

² D. C. Henry, *Phil. Mag.*, (6), 1922, **44**, 689.

for a given solid and r_0 is the mean value of the distance through which the attractive forces are operating,

$$E = \mu a_s^{\frac{1}{2}} a_g^{\frac{1}{2}} \varphi(r_0) \quad . \quad . \quad . \quad . \quad (3)$$

Combining (2) and (3), we may reach the expression for the isostere

$$\log \frac{x}{c} = K_1 + \frac{K_2}{T} \quad . \quad . \quad . \quad . \quad (4)$$

or, expanding this by Taylor's theorem and taking first terms, we get the isotherm for adsorption up to about 30 per cent of the saturation value

$$\log \frac{x}{c} = k_1 + k_2 x \quad . \quad . \quad . \quad . \quad (5)$$

An example of the applicability of Williams' isostere to experimental data is given in fig. 147¹ which embraces Miss Homfray's data for sorption by charcoal.

Williams observed such good agreement between the best available experimental data and his isostere formulation (4) that he found it unnecessary to assume an appreciable temperature coefficient for the expression (3) or the range of molecular attraction δ . The isotherm agrees with Chappuis' accurate data for the sorption of carbon dioxide by charcoal over a very wide range within a small fraction of one per cent.² Experimental error is enormously exaggerated at low initial pressures because the transition to Henry's law at infinitesimal pressures is implicit in the formula.

The values of K_2 were found to be, as predicted, parallel to the square root of a from van der Waals' equation. Taking the values of a and b from van der Waals' equation and assuming that r_0 and δ are appreciably the same for the series of gases used in Miss Homfray's sorption experiments on charcoal, examination of the significance of the constant K_2 of the isostere yields a value of δ equal to 3.2 to 4.1 Å. and an area per kilogram of unactivated charcoal of 131,000 square metres. A value of $\delta = 4$ Å. is, however, a remarkable

¹ A. M. Williams, *Proc. Roy. Soc. (London)*, A, 1919, **96**, 300, fig. 5.

² See also, for example, S. J. Gregg, *J. Chem. Soc.*, **1927**, 1494.

demonstration that adsorption even in charcoal is monomolecular. Only in the case of charcoal exposed to the

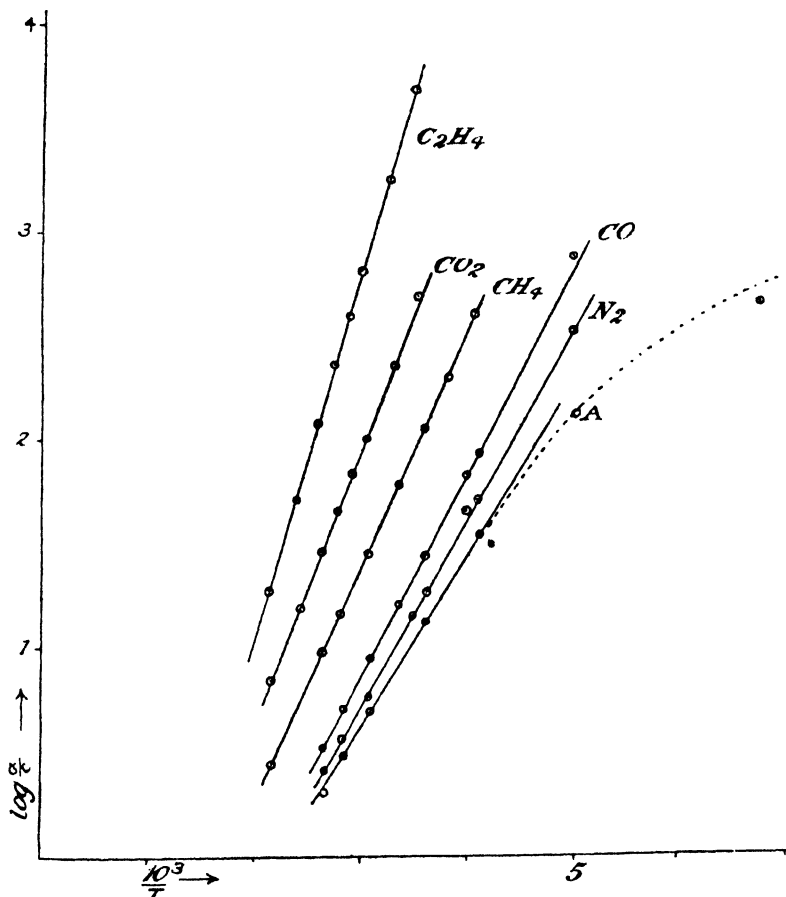


Fig. 147.—Comparison of Miss Homfray's Data for Sorption of various Gases by Charcoal with the Straight Lines demanded by the Williams Isostere.

saturated vapour of liquid argon did the observed values of sorption exceed that for one molecule deep, and results with *saturated* vapours are, of course, of quite indefinite significance.

It may be added that Williams' isostere predicts an upper temperature limit for observable adsorption.

Scrutiny of the assumptions made by Williams shows that his equations are the exact equivalent of those based upon the Boltzmann distribution law as employed by so many authors (see page 483, footnote 3).¹

The derivation of an adsorption isotherm by Henry² may be referred to as the "fly-paper" hypothesis. He begins with the assumption that adsorption is monomolecular, and then attains the equivalent of the assumption used by most writers and referred to in the preceding paragraph as well as by Williams (uniform thickness of sorption volume and continuous distribution of attractive forces over the surface) by assuming that a molecule is held by many elementary spaces—like a fly on numerous sticky points small in comparison with the size of the fly.

It is interesting and significant that these premises should, following the line of reasoning used by Langmuir, lead to an isotherm and an isostere identical in form with that of Williams. Applying it to the data for simple gases and vapours sorbed on charcoal, values of from 3.2 to 5.8 elementary spaces per molecule were deduced, the smallest being for nitrogen and the largest for chloroform.

EXTENSION TO THE THEORY OF SURFACE FILMS

By means of a simple isothermal cycle process Volmer³ shows that the equation of state for a surface film,

¹ See also H. Freundlich, *Kapillarchemie*, 1930, Bd. I, p. 187; M. Dunkel and H. Mark, *Monatsh.*, 1929, **53-54**, 764; W. Sementschenko, *Z. physik. Chem.*, 1927, **129**, 176.

² D. C. Henry, *Phil. Mag.*, (6), 1922, **44**, 689.

³ M. Volmer, *Z. physik. Chem.*, 1925, **115**, 253. K. C. Kar and A. Ganguli (*Physik. Z.*, 1929, **30**, 920) criticize Volmer's reasoning on the ground that it is based partly upon thermodynamics and partly upon mechanics; consistent reasoning would have led exactly instead of approximately to Langmuir's formula. M. N. Chakravarti and N. R. Dhar (*Kolloid-Z.*, 1927, **43**, 377; 1928, **45**, 12) deduce a formula somewhat like Langmuir's but containing an exponent $1/n$ where n is the number of elementary spaces occupied by a sorbed molecule.

$\pi(\Omega - \beta) = RT$, is equivalent to an adsorption formula identical in form with that of Langmuir for moderate amounts of adsorption,

$$\eta = \frac{c}{k + 2\beta c}.$$

In these equations π is the difference in surface tension between the original uncontaminated surface and that carrying the adsorbed layer; this was formerly always referred to as the lowering of surface tension through adsorption. Ω is the area (or adsorption volume) adsorbing one gram mol of gas obeying the perfect gas laws. β is equal to twice the actual cross sectional area of N molecules. Hence each molecule occupies, on account of thermal vibration, a surface equal to 2β ; namely, four times its own area. This correction is exactly analogous to that introduced in the van der Waals equation for the difference in the actual and effective volume of molecules in a gas. A close packed layer of molecules therefore covers only one quarter of the surface at a given moment. Hückel¹ points out that Langmuir allowed in a measure for this effect by comparing the maximum number of sorbed molecules upon a surface with that of a similar film of liquid. η is the amount of adsorption in gram mols per square centimetre, c is the concentration in the gaseous phase, and k is a constant.

Garner² expressed the opinion that the simple Langmuir equation would not hold when the lateral attraction between the molecules in the film plays a large part in its stability. Langmuir³ found that for the monatomic adsorption of caesium upon tungsten the equation of state of the two-dimensional gas corresponded to that of an ideal gas, at least until 20 per cent of the surface was covered. In certain more concentrated films attractive forces between the caesium atoms bring about the separation of a second distinct concentrated surface phase.

¹ E. Hückel, *Adsorption und Kapillarkondensation*, 1928, p. 150.

² W. E. Garner, *Trans. Faraday Soc.*, 1926, **22**, 459.

³ I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc. (London)*, A, 1925, **107**, 70.

Semenoff¹ applies in full the two-dimensional surface analogue of the van der Waals equation

$$\left(\pi + \frac{a}{\Omega^2}\right)(\Omega - \beta) = RT$$

which should lead to discontinuities in the observed sorption isotherms. He contemplates polymolecular as well as monomolecular adsorption. His formulation, derived statistically for static conditions, agrees with that of Frenkel deduced kinetically.

To the long list of those who have deduced an equation similar to that of Langmuir may be added Kobayashi,² who assumed that the adsorbed layer behaves as a two-dimensional gas, its molecules possessing a small vibration perpendicular to the surface,

$$\eta = \frac{(\theta/\omega)c}{1 + \theta c}$$

where θ contains λ as a function of temperature, λ representing the mean free path for translational motion of the adsorbed mols, and w is the area occupied by an adsorbed mol.

LAMINATED OR ENCHAINED MULTIMOLECULAR FILMS

Many writers³ have had the conception that adsorbed material may consist of a series of superimposed monomole-

¹ N. Semenoff, *Z. physik. Chem.*, Abt. B, 1930, **7**, 471; compare A. Frumkin, *Z. physik. Chem.*, 1925, **116**, 466. A. Magnus (*Z. anorg. allgem. Chem.*, 1926, **158**, 67; *Z. Elektrochem.*, 1928, **34**, 531) developed a formula resembling van der Waals' but with repulsive instead of cohesive forces on the ground that similarly oriented dipoles must repel each other and hence a must have a negative sign (see also E. Hückel).

² Y. Kobayashi, *Chem. News*, 1929, **139**, 153; *Bull. Inst. Phys. Chem. Research (Tokyo) Abstracts*, 1929, **2**, 71.

³ For example, this view was put forward by R. A. Smith in 1863 (see *Proc. Roy. Soc. (London)*, A, 1926, **112**, 301); H. Kayser, *Wied. Ann. der Physik*, 1881, **14**, 463; see also A. B. Lamb, R. E. Wilson and N. K. Chaney, *J. Ind. Eng. Chem.*, 1919, **11**, 424; I. Langmuir, *Trans. Farad. Soc.*, 1921, **17**, 614; this chapter, pages 465 and 466; W. W. Hurst and E. K. Rideal, *J. Chem. Soc.*, 1924, **125**, 703 (who assumed from 8 to 13 layers of the polar carbon monoxide as compared with a single

cular layers each adsorbed upon that immediately beneath. It is clear that this mechanism is wholly different from that assumed to be due to long range attractive forces as in the classical compressed film theory discussed in Chapter XVII.

This mechanism in the extreme case for non-volatile substances or nearly saturated vapours could easily lead to films of indefinite thickness. Thus Bartsch¹ considered that he had built up 9,500 molecular layers of oleic acid upon copper pyrites.

de Boer and Zwikker² have examined this hypothesis in quantitative detail for the sorption of iodine molecules by crystals of calcium fluoride, where up to 30 layers appear to have been observed in nearly saturated vapour. Such adsorption can be continued in more than one layer of iodine by dipole induction only as long as the molecules are close enough together. It would not be possible for rather widely separated permanent dipoles, such as fatty acids. The brown colour of the adsorbed iodine layer is attributed to the result of polarization.

Tanner³ has suggested another mode of formation of a film exceeding one molecule deep which might be called a monoparticulate layer. He suggests that a nearly saturated vapour contains liquid nuclei or embryonic droplets which would accordingly be strongly adsorbed and probably stabilized thereby; hence they might form a more or less complete

layer of the non-polar hydrogen; others, however, have used the same data as evidence for active patches); E. K. Rideal, *Nature*, 1926, **117**, 627, who compares such attraction with that of a magnet on a string of iron filings; F. G. Keyes and M. J. Marshall, *J. Am. Chem. Soc.*, 1927, **49**, 156, who especially emphasize it. However, A. F. H. Ward and E. K. Rideal (*J. Chem. Soc.*, 1927, 3127) suggest that the actual observations which led the latter to advance this view were quite insufficient and that, instead of having a multimolecular film, they were not dealing with sufficient adsorption to account for more than a few per cent of a monomolecular layer.

¹ O. Bartsch, *Kolloid-Z.*, 1926, **38**, 325.

² J. H. de Boer, *Physica*, 1928, **8**, 145; J. H. de Boer and C. Zwikker, *Z. physik. Chem.*, Abt. B, 1929, **3**, 407.

³ J. W. McBain and H. G. Tanner, *Proc. Roy. Soc. (London)*, A, 1929, **125**, 585.

monoparticulate film of these molecular clusters polarized throughout by the surface to which they are attached.

GENERAL CONCLUSIONS

It is clearly evident that the theory of Langmuir has been triumphantly successful in every case which might be classified as chemisorption and that, for all cases, extremely varied modes of theoretical attack have led to general conclusions identical in form and significance with his analysis. The classical thick compressed film theory necessitates long range attractive forces whose existence is not envisaged in modern conceptions of the electrical structure of matter. There remains, of course, the possibility that such forces are yet to be discovered.¹

The attempt to transfer from the classical thick compressed film hypothesis the use of the ordinary equation of state with its ordinary constants to a monomolecular film, is not justifiable if the attractive centres are sufficiently localized on the surface, especially if the distance between them is comparatively great when compared with the dimensions of the molecule to be sorbed. At a sufficiently high temperature, the behaviour of the molecules will conform closely to that of the ordinary gas equation.² Such considerations presumably account for the disproof by McBain and Britton³ of this mode of interpretation of monomolecular adsorption in the case of nitrogen and charcoal. Furthermore, the enormous attractive forces of the solid are not exerted either in the plane of the film or wholly at right angles to it.

However, the Langmuir hypotheses have been greatly enriched by the proof that under certain conditions adsorbed films may exist in the form of two-dimensional mobile phases.

¹ See the remarkable results of W. B. Hardy and M. Nottage, Chapter X, pp. 348–351.

² For example, in Davisson and Germer's experiments (see Chapter IX, page 322) hydrogen atoms upon nickel conformed precisely to the spacings of the crystal lattice up to temperatures of 150° C.

³ J. W. McBain and G. T. Britton, *J. Am. Chem. Soc.*, 1930, **52**, 2198.

CHAPTER XIX

EVIDENCE FROM CONTACT CATALYSIS AS TO THE NATURE OF SORPTION

EFFECT OF THE CONCEPTION OF MONOMOLECULAR ADSORPTION

The subject of heterogeneous or contact catalysis as classified and illustrated by Berzelius and Faraday remained for generations a bewildering mystery. Schönbein confessed that the word catalysis was a synonym for ignorance, and it was a great step forward when, at the opening of the present century, Wilhelm Ostwald referred all the observations to measurements of rate of reaction in the way exemplified by the systematic studies of Bodenstein and his collaborators.

A number of investigators such as Bodenstein and Fink suggested possible mechanisms, but more than anyone else Langmuir has influenced the development of this subject by a clear-cut picture of the actual happenings in a particular type of reaction. His deductions are all based upon observable factors, each independently measurable. The very complexity which is so baffling has been utilized to display the interaction of simple principles.

The subject of contact catalysis is so much in the forefront of attention, is undergoing so extensive a development and elucidation, and is being so often and well surveyed by specialists that it is unnecessary for our purpose to do more than show in detail by one or two examples how the conception of monomolecular adsorption provides a sufficient key to the varied behaviour of particular cases. Then we may proceed to refer to other hypotheses used in this field and any additional information gathered with regard to sorption as such.

For current summaries of the subject of contact catalysis for its own sake, reference may be made to the Annual Reports

of the American Committee on Contact Catalysis of the Division of Chemistry and Chemical Technology of the National Research Council and to reviews in various journals and books.¹

An important study of the contact process for sulphur trioxide was made by Bodenstein and Fink in 1907.² Finding the rate of reaction inversely proportional to the square root

¹ Eight annual reports: (1) W. D. Bancroft, *J. Ind. Eng. Chem.*, 1922, **14**, 326, 444, 545, 642; *Reprint and Circular Series of the National Research Council*, 1922, No. 30. (2) W. D. Bancroft, *J. Phys. Chem.*, 1923, **27**, 801; *Reprint and Circular Series of the National Research Council*, 1923, No. 50. (3) H. S. Taylor, *J. Phys. Chem.*, 1924, **28**, 898; *Reprint and Circular Series of the National Research Council*, 1924, No. 59. (4) H. S. Taylor, *J. Phys. Chem.*, 1926, **30**, 145; *Reprint and Circular Series of the National Research Council*, 1926, No. 66. (5) E. Emmet Reid, *J. Phys. Chem.*, 1927, **31**, 1121; *Reprint and Circular Series of the National Research Council*, 1927, No. 78. (6) R. E. Burk, *J. Phys. Chem.*, 1928, **32**, 1601; *Reprint and Circular Series of the National Research Council*, 1928, No. 83. (7) E. F. Armstrong and T. P. Hilditch, *J. Phys. Chem.*, 1929, **33**, 1441; *Reprint and Circular Series of the National Research Council*, 1929, No. 90. (8) J. C. W. Frazer, *J. Phys. Chem.*, 1930, **34**, 2129; *Reprint and Circular Series of the National Research Council*, 1930, No. 94. Other recent reviews: E. Sauter, *Heterogene Katalyse. Ergebnisse der neueren Entwicklung der chemisch-physikalischen Erforschung der durch Grenzflächen beschleunigten chemischen Reaktionen*, Bd. XXIII der Sammlung Wissenschaftliche Forschungsberichte (Th. Steinkopff, Dresden, 1930); E. Sauter, *Z. Elektrochem.*, 1930, **36**, 874; *Kolloid-Z.*, 1928, **46**, 148; 1929, **49**, 450; E. K. Rideal and H. S. Taylor, *Catalysis in Theory and Practice* (Macmillan & Co., Ltd., London, 1926); T. P. Hilditch, *Catalytic Processes in Applied Chemistry* (Chapman & Hall, Ltd., London, 1929); C. N. Hinshelwood, *The Kinetics of Chemical Change in Gaseous Systems* (The Clarendon Press, Oxford, 1929); G. M. Schwab, *Ergebnisse der exakten Naturwissenschaften*, 1928, **7**, 276; W. Frankenburg, *Z. angew. Chem.*, 1928, **41**, 523, 561. A systematic index to the older literature is provided by G. Woker, *Die Katalyse*, Bd. I and II Abt. 1, *Die chemische Analyse*, Bd. XI, XII, XXI, and XXII (F. Enke, Stuttgart, 1910 and 1915). Two further reviews are announced: H. S. Taylor, *Chem. Reviews*, 1931, **8**, June; Wo. Ostwald, *Kolloid-chem. Beihefte*, 1931, **32**, 1.

² M. Bodenstein and C. G. Fink, *Z. physik. Chem.*, 1907, **60**, 1; I. Langmuir, *J. Am. Chem. Soc.*, 1915, **37**, 1139; 1916, **38**, 2287; *Trans. Farad. Soc.*, 1922, **17**, 621.

of the concentration of sulphur trioxide, they suggested that the reacting substances had to diffuse through a thick sorbed film of this product of reaction. Langmuir long after pointed out that the rate may vary a thousand or even a million fold but that this can hardly be true of the thickness of the film which Bodenstein and Fink found not to exceed 12 Å. even when referred to the visible area of a surface that was in reality pitted. Recently¹ Bodenstein re-interpreted this in terms of a mobile monomolecular adsorbed film.

Langmuir sought explanations in terms of monomolecular adsorption and suggested the following three mechanisms as possibilities in various cases :

(a) Atoms² or molecules adsorbed on adjacent spaces may react and be desorbed together. Examples of such action occur between hydrogen and oxygen adsorbed on platinum.

(b) An atom or molecule of the adsorbed layer may react with the underlying solid. An example of this is to be found in carbon dioxide sorbed on the oxides of copper and magnesium.³

¹ M. Bodenstein, *Z. physik. Chem.*, Abt. B, 1929, **2**, 345.

² Langmuir early postulated that many diatomic molecules are adsorbed as atoms. See also H. S. Taylor (*Proc. Roy. Soc. (London)*, A, 1926, **113**, 77) and M. Polányi (*Z. Elektrochem.*, 1929, **35**, 561). Activation by adsorption was suggested by M. Polányi (*Z. Elektrochem.*, 1921, **27**, 142); compare H. S. Taylor and G. B. Kistiakowsky (*Z. physik. Chem.*, 1927, **125**, 341) and G. M. Schwab and E. Pietsch (*Z. physik. Chem.*, 1927, **126**, 473). A. W. Porter (*Nature*, 1930, **126**, 349) shows how the normal energy of activation required to make a collision effective in the gaseous condition may be retained unaltered in the adsorbed condition and yet, owing to suitable orientation towards molecules approaching from the gaseous phase, may multiply the catalytic activity by a factor of the order of 10⁸. Andrews (quoted by J. C. W. Frazer, *J. Phys. Chem.*, 1930, **34**, 2155) points out that an adsorbed molecule may be activated through the momentary concentration of energy in some particular bond. Most recent writers stress chemisorption as the essential of activation of adsorbed material.

³ W. M. Hoskins and W. C. Bray, *J. Am. Chem. Soc.*, 1926, **48**, 1454; J. A. Almquist and W. C. Bray, *J. Am. Chem. Soc.*, 1923, **45**, 2305; W. C. Bray and G. J. Doss, *J. Am. Chem. Soc.*, 1926, **48**, 2060. But see the divergent explanation given by W. A. Bone and G. W. Andrew (*Proc. Roy. Soc. (London)*, A, 1925, **109**, 459; 1926, **110**, 16; W. A. Bone, *Proc. Roy. Soc. (London)*, A, 1926, **112**, 474). Their

(c) An adsorbed atom or molecule may be struck by a molecule from the gaseous phase and react with it either immediately or after double adsorption. This will be illustrated in detail for the oxidation of carbon monoxide on platinum.¹

THE MECHANISM OF THE OXIDATION OF CARBON MONOXIDE ON PLATINUM SURFACES

Faraday in enumerating various substances which in traces prevent or poison this catalysis found that carbon dioxide had but little effect. The other poisons are known to be tenaciously adsorbed. The rate of reaction is found empirically to be subject to very different rules at different temperatures. Two examples will be taken for illustration :

(a) At 0.1 mm. pressure and 200° to 400° C. the rate is proportional to the pressure of the oxygen but inversely proportional to that of the carbon monoxide. The temperature coefficient is 1.6 for 10°.

(b) At 500° to 800° C. the rate is independent of the temperature. When oxygen is present in excess, the rate is proportional to the pressure of the carbon monoxide. When carbon monoxide is in excess, the rate is proportional only to the pressure of the oxygen.

Carbon dioxide is not much sorbed by platinum. Carbon monoxide is strongly but reversibly sorbed. Oxygen is so strongly sorbed that it is retained even upon heating to 1,200° C.

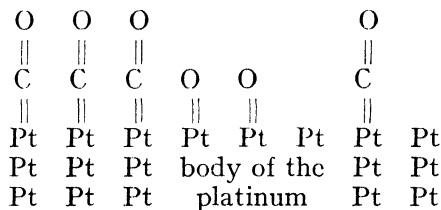
The whole of the complicated behaviour of this reaction of which two examples have been given was shown by Langmuir to follow directly from three simple and highly plausible assumptions.

(1) Carbon monoxide molecules are oriented so that the carbon atom is held to the platinum, and the oxygen with its valencies already saturated is exposed to the gas. Such

explanations do not agree with any of Langmuir's suggestions but involve complexes, and they emphasize the important influence of moisture.

¹ I. Langmuir, *Trans. Farad. Soc.*, 1922, **17**, 621 ; see also page 607 of this reference.

carbon monoxide molecules do not react with oxygen molecules which strike them.¹ In due course an adsorbed molecule of carbon monoxide is again desorbed, leaving a vacant space. Whilst it is upon the surface it acts as a poison, for it renders the spot it covers unavailable for reaction.



(2) Oxygen and carbon monoxide molecules arriving from the gaseous phase compete for any vacant spaces, first come first served.

(3) A carbon monoxide molecule arriving from the gas, upon striking an adsorbed oxygen atom reacts with it to form carbon dioxide, which is then desorbed.

At 300° C. the surface is largely covered with carbon monoxide. The rate is therefore proportional to the oxygen, competing for its share of vacant spaces, and inversely proportional to the carbon monoxide which uselessly monopolizes those it captures.

With rising temperature, as the surface is set free from carbon monoxide, the rate increases. The temperature coefficient is then a fraction of the heat of desorption of carbon monoxide, which simulates a heat of activation of 31,800 calories. At 400° C., above which the surface is becoming largely uncovered, carbon monoxide is no longer a poison, especially at low partial pressures. It is directly required for union with oxygen on the surface, but its rate of arrival is limited by the Hertz-Knudsen effusion equation which

¹ H. R. Kruyt (*Z. Elektrochem.*, 1929, **35**, 539) summarizes his own work, showing that if the reactive group is sorbed, the reaction is slowed and vice versa. Monomolecular reactions are slowed. Compare H. R. Kruyt, and C. F. van Duin, *Rec. trav. chim.*, 1921, **40**, 249.

indeed sets a limit to each gas separately. Hence the temperature coefficient becomes negligible.

At a red heat, if carbon monoxide is in large excess, the rate is dependent only upon the arrival of oxygen upon the surface, to be promptly struck and removed as carbon dioxide. Here the rate is governed solely by the effusion formula, applied to the oxygen. With oxygen in excess, the same formula governs the rate but now refers only to the carbon monoxide.

At a white heat, so small a part of the surface is covered that the temperature coefficient is negative, the rate being only one-sixth that at red heat. The rate is proportional both to the carbon monoxide and to the oxygen, both favouring an effective collision upon the surface.

Thus with a very simple and consistent mechanism, full and quantitative account is given of the manifold changes in the factors governing the rate and the apparent vagaries according to which a gas may hinder or promote or be indifferent to the rate of its reaction at the surface.

This one example may serve to illustrate the astonishing change in the outlook upon contact catalysis brought about by the introduction of the conceptions of monomolecular adsorption, and the power of this hypothesis, especially when reinforced by the possibilities of mobility upon the surface, multiple adsorption, dissociation into atoms, and other developments of the monomolecular hypotheses already mentioned. Specific effects have almost of necessity to be explained upon the basis of monomolecular adsorption.

ACTIVE PATCHES OR CENTRES

Study of catalysis rendered a distinct contribution to the subject of sorption when it was shown by many investigators that traces of poison reduce the catalytic activity far more than they affect the sorptive power of a catalyst.¹ For

¹ E. B. Maxted, *J. Chem. Soc.*, 1919, **115**, 1050; 1920, **117**, 1280, 1501; 1921, **119**, 225, 1280; E. F. Armstrong and T. P. Hilditch, *Trans. Farad. Soc.*, 1922, **17**, 670; R. N. Pease, *J. Am. Chem. Soc.*, 1923, **45**, 1196, 2235; R. N. Pease and L. Stewart, *J. Am. Chem. Soc.*, 1925, **47**, 1235; and many others (see, for example, H. S. Taylor, *J. Phys. Chem.*, 1926, **30**, 145).

example, Pease and Stewart showed that the sorption of carbon monoxide on a copper catalyst reduced the rate of hydrogenation of ethylene to 15 per cent of the normal value, although the sorptive capacity for hydrogen and ethylene was many hundred fold the volume of carbon monoxide used. Evidently the amount of poison is far too small to cover the surface.

It has been shown that colloidal platinum can be progressively poisoned by successive additions of carbon disulphide so that the rates of hydrogenation of a number of organic compounds one by one become negligible.¹

It is thus clearly shown that all portions of the "surface" of an amorphous or colloidal catalyst are not equivalent from either the standpoint of catalysis or of sorption. This state of affairs was clearly described by Langmuir² in 1916.

"It is evident that with a structure of this kind it is meaningless to talk about the surface on which adsorption can take place. With plane surfaces, we have seen that adsorption is usually limited to the formation of a layer one molecule deep, so that we can estimate the maximum adsorption from the extent of the surface. With charcoal, on the other hand, there is no definite surface which can be covered by a layer one molecule deep. Between the atoms of carbon, there must be spaces of all possible sizes and shapes, some just too small to hold a gas molecule, others big enough to hold one but not hold two, etc. There are some spaces in which a molecule would be closely surrounded by carbon atoms on nearly all sides, whereas in other places a molecule would be able to hold on to only a single carbon atom. Under these conditions there will be some spaces from which it would take place much more rapidly. There would be, however, a fairly sharp limit to the number of molecules which could come into intimate contact with carbon atoms. This limit would correspond to the saturated state observable in adsorption even by porous bodies."

The conception of active patches was introduced to general recognition by H. S. Taylor³ and has been the inspiration

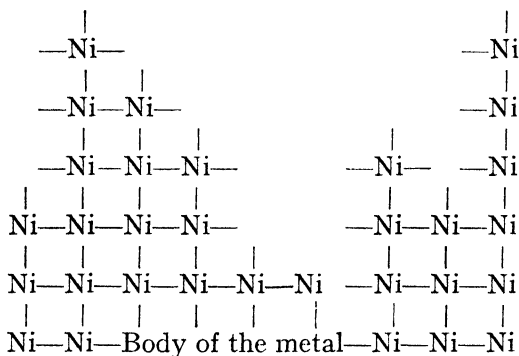
¹ G. Vavon and A. Husson, *Compt. rend.*, 1922, **175**, 277.

² I. Langmuir, *J. Am. Chem. Soc.*, 1916, **38**, 2286.

³ H. S. Taylor, *Proc. Roy. Soc. (London)*, A, 1925, **108**, 107; M. Volmer, *Z. physik. Chem.*, 1925, **115**, 260.

of much of the work of his school. This point of view was especially well developed in the Fourth Report on Contact Catalysis.¹

Taylor's diagram of the surface of a nickel catalyst differs from those previously given in that it shows many peaks and valleys upon the exterior.



A nickel atom upon a peak may be held by only one bond and is thus almost like atomic nickel with all the other valencies exposed and available for chemical combination or adsorption. It is evident that different points upon such a surface are not equivalent² and Taylor emphasizes especially the activity of the exposed atoms upon the peaks. The most active points are expected to adsorb first and the heat of adsorption would vary with the amount adsorbed.

Armstrong and Hilditch³ carry Taylor's hypothesis one step further and assume that when a fully exposed nickel

¹ H. S. Taylor, *J. Phys. Chem.*, 1926, **30**, 145. For a good brief review of the work of Taylor and his collaborators on catalysis, see H. S. Taylor, *Z. Elektrochem.*, 1929, **35**, 542.

² A good example is supplied by R. W. Wood (*Proc. Roy. Soc. (London)*, A, 1922, **102**, 1) who found that on clear glass hydrogen atoms combine but slowly, whereas if the surface upon which they are deposited is scratched, the scratch becomes incandescent.

³ E. F. Armstrong and T. P. Hilditch, *Proc. Roy. Soc. (London)*, A, 1925, **108**, 111, 121; *Chem. and Ind.*, 1925, **44**, 701; Institut International de Chimie Solvay, Deuxième Conseil tenu à Bruxelles (avril 1925).

atom captures hydrogen and unsaturated organic molecules by different valencies, the complex may become wholly detached and subsequently break up by one of several paths, the nickel generally being redeposited on some exposed point. Armstrong's treatment forms an effective bridge between adsorption and pure chemistry.

Taylor and Armstrong's views would account for the pitting¹ which occurs during the use of certain catalysts, the effects of heat treatment, the function of the support such as asbestos or pumice upon which the catalyst is spread,² in addition to many specific effects such as the possibility of poisoning a catalyst for an undesired side reaction. However, reference to previous chapters such as IX and XIII shows that this is not necessarily the sole explanation of some of these effects. Thus disintegration may be caused by mere sorption and desorption, and heating may affect the whole material and not merely active centres.³

Donnelly and Hinshelwood⁴ point out that the presence of centres of different activity would account for a change in the laws governing the interaction of hydrogen and oxygen on a platinum surface at high and low pressures, respectively.

ADLINEATION

Langmuir⁵ showed that it followed from his conceptions of the mechanism of adsorption that when separate phases of constant composition were present, as in the decomposition of a solid such as calcium carbonate, the reaction must take place exclusively at the boundary of these phases. This kinetic interpretation of the phase rule indicates clearly the

¹ W. A. Bone and G. W. Andrew (*Proc. Roy. Soc. (London)*, A, 1925, **109**, 459) find that pitting does not occur during the catalysis of the reaction between carbon dioxide and oxygen at a gold surface, the gold remaining smooth indefinitely.

² R. Dankoff (*Nature*, 1930, **126**, 860) obtained highly active deposits of nickel, platinum and iron on glass at 0° and — 180° by condensation of their vapours at a pressure of 10⁻⁵ mm.

³ Compare F. H. Constable, *J. Chem. Soc.*, **1927**, 1578.

⁴ R. P. Donnelly and C. N. Hinshelwood, *J. Chem. Soc.*, **1929**, 1727.

⁵ I. Langmuir, *J. Am. Chem. Soc.*, 1916, **38**, 2263.

distinction between reactions in which solid solutions are formed and those in which separate phases appear. This theory offers a ready explanation for the fact that some hydrated crystals fail to effloresce unless scratched, and for the fact that thoroughly dehydrated substances will absorb water only with difficulty.

This same conception applies to two-dimensional systems and has been extensively developed by recent writers.

The increasing recognition of edges, points and the spontaneous fractures¹ and imperfections of all crystal surfaces as being specially active centres or points is discussed by Stranski² who gives a table of energies for particular locations.

A discussion of the development of this subject has been given by Schwab and Pietsch,³ with eighty-six references.

HEATS OF SORPTION, ACTIVATION AND RATE

Taylor is studying especially the connexion between heats of sorption, heats of activation and rates of catalysis, which he illustrates in the following sentences.⁴ Dew's observations upon the adsorption of ammonia by copper, nickel and iron show that all three heats of adsorption run parallel, that with iron being about 5,000 calories greater than that with nickel and about 7,000 calories greater than that with copper. If for the sake of simplicity we assume a monomolecular decomposition and the same energy of activation for these three catalysts, the rate with iron will be greater than that with nickel in the proportion of $e^{\frac{5,000}{RT}}:1$ and $e^{\frac{7,000}{RT}}:1$ greater than

¹ For glasses, A. A. Griffith, *Trans. Roy. Soc. (London)*, A, 1920, **221**, 163; for crystals, A. Smekal, *Wien Anz.*, 1925, pp. 159, 191; *Physik. Z.*, 1925, **26**, 707; *Z. Physik*, 1927, **45**, 869; 1929, **55**, 289; *Z. Elektrochem.*, 1928, **34**, 472; 1929, **35**, 567; *Z. physik. Chem. Abt. B*, 1929, **5**, 60, etc., etc.; F. Zwicky, *Proc. Nat. Acad. Sci.*, 1929, **15**, 253, and many other writers.

² I. N. Stranski, *Z. Elektrochem.*, 1930, **36**, 25.

³ G. M. Schwab and E. Pietsch, *Z. Elektrochem.*, 1929, **35**, 573; *Z. physik. Chem.*, 1927, **126**, 473; E. Pietsch, A. Kotowski and G. Berend, *Z. Elektrochem.*, 1929, **35**, 582.

⁴ Translated from H. S. Taylor, *Z. Elektrochem.*, 1929, **35**, 548. Compare B. Topley, *Nature*, 1931, **128**, 115.

that of copper. At 800° absolute the rates of reaction will therefore be in the proportion 20 : 1 and 90 : 1. The velocity with iron would be greater than with a non-specific adsorbent for which the heat of sorption is about equal to the heat of condensation, in the ratio $e^{\frac{16,000-6,000}{RT}}$: 1. At 800° absolute this ratio is $e^{6.25}$: 1.

PROMOTERS

Out of the attempts to replace expensive, pure metallic catalysts by cheaper diluents, substitutes, and supports arose the discovery that many additions, in themselves not particularly good catalysts, greatly enhance the catalytic activity by their presence. These are called promoters (Verstärker oder Aktivatoren) and have been extensively studied since 1910 by Mittasch and his collaborators of the Badische Anilin- und Soda-Fabrik.¹

The action of promoters is explicable in terms of the conception of active patches or centres. If the surface of a catalyst is not a checkerboard of equipotential points but consists of portions of minute crystal edges, corners and imperfections in addition to numerous skeletal chains of atoms awaiting the opportunities provided by thermal agitation for slipping into the more compact crystal lattice, both the interatomic distances as well as the number and variety of atoms around one particular atom will affect not merely the facility but also the kind and efficacy of adsorption. It is then understandable that the variation in the closeness of packing as well as an introduction of foreign elements frequently alters the rate and direction of reaction.

“There appear to be at least three different types of such active surfaces on carefully prepared nickel : on one all hydrogenation reactions, including saturation of ring compounds, may be performed ; on a less active area, simple double bonds undergo hydrogenation but not ring compounds ; and a third area facili-

¹ Numerous patent references ; see A. Mittasch, *Ber.*, 1926, **59B**, 13 ; also for survey, H. Brückner, *Katalytische Reaktionen in der organisch-chemischen Industrie*, Part. I. (Band XXII der Sammlung “Technische Fortschrittsberichte”, Th. Steinkopff, Leipzig, 1930).

tates only the reduction of nitro groups. In the case of carbon containing both iron and nitrogen, there exists a large area, inactive catalytically, for the oxidation of oxalic acid; but in addition there exist areas of active carbon, active carbon-nitrogen, active carbon-nitrogen-iron and active carbon-iron complexes; these all possess different specific surface activities and different temperature coefficients for the reaction velocities."¹

Balandin² has gone farthest in formulating a precise conception of active patches and favourable spacings, even on smooth crystal surfaces. His ideas are likewise a development of the conception of multiple adsorption, as already discussed by others.³ He also assumes that a single active spot has the power of attracting different atoms of the same molecule. The formation of ethylene from alcohol is explained by assuming that hydroxyl and hydrogen are strongly adsorbed by one spot and the two carbon atoms by another, the first part being desorbed as water, the remainder as ethylene. On the other hand, where one spot adsorbed two hydrogen atoms and the other neighbouring active spot holds the remainder of the molecule, upon desorption the alcohol will be dehydrogenated with formation of aldehyde. He explains the exclusive formation of benzene upon platinum from hexamethylene. The surface of the platinum space lattice consists of a series of triangles. If each corner attracts two

¹ E. K. Rideal, *Nature*, 1926, **117**, 627; E. K. Rideal and W. M. Wright, *J. Chem. Soc.*, 1925, **127**, 1347; **1926**, 1813. Apart from the very extensive industrial literature these points of view are of great biological importance in characterizing reactions in cells and the actions of enzymes. See, for example, O. Warburg and W. Brefeld, *Naturwissenschaften*, 1923, **11**, 862; *Biochem. Z.*, 1924, **145**, 461; J. Duclaux, *Deuxième Cons. Chim. Inst. Intern. Chimie Solvay*, 1926, p. 630. Animal charcoal is more effective than ozone in oxidizing tincture of guaiacum but after extraction of iron with strong hydrochloric acid, it, like wood charcoal, has no effect. J. R. Dupouy, *Pharm. Zentralhalle*, 1897, **38**, 705; *Répert. Pharm.*, 1897, p. 396; V. Podrouzek, *Chem. Listy*, 1926, **20**, 553.

² A. A. Balandin, *Z. physik. Chem.*, Abt. B, 1929, **2**, 289; 1929, **3**, 167.

³ R. E. Burk (*J. Phys. Chem.*, 1926, **30**, 1134) used the hypothesis of multiple adsorption to explain the action of promoters, poisons and active centres.

of the carbon atoms of the ring, there will be three neighbouring platinum atoms, each in a position to hold or pull away two atoms of hydrogen from the molecule. Five or seven membered ring compounds could not fit this crystal lattice and therefore could not be hydrogenated in this way. From the data of the size of various atoms and their distances apart on the surface, he calculates that the atoms only of certain metals could be catalytically active.

It will be seen that throughout the whole of this chapter the distinctive evidence provided by the subject of contact catalysis supports and greatly enriches the conception of monomolecular adsorption. This is evidently the mechanism of at least the majority of such reactions. However, the fact that this selected group of sorptions falls within this category would not in itself exclude the possibility that longer range forces might be discovered for other cases such as those suggested by Hardy.

CHAPTER XX

ELECTRICAL INTERPRETATION OF SORPTION

FORCES AT PRESENT RECOGNIZED

Current science recognizes no long range forces such as were universally accepted in classical physics ¹ but restricts significant interactions between molecules or atoms to a range of a few Ångstrom units and assumes that they fall off very rapidly with the distance. In order to explain the many kinds of chemical combination and cohesion, adhesion, sorption and van der Waals' forces we have left only the coupling of spinning electrons (homopolar bond) and electrostatic attractions. Chemists distinguish amongst their compounds ionic or polar compounds such as sodium chloride, heteropolar compounds, such as hydrochloric acid,² water or ammonia, co-ordinated compounds,³ free radicals and unsaturated compounds, addition compounds, associated molecules, compounds due to residual valence such as hydrate water, etc., etc. In addition to these we have all the manifestations of physical attraction such as physical adsorption and van der Waals' forces. The application of wave mechanics to this subject is hitherto quite disappointing because it has only recognized attractive forces at distances far shorter than those involved in cohesion, van der Waals' forces and physical adsorption in spite of the universal occurrence and importance of the latter.

¹ But see the experiments of W. B. Hardy and others (Chapter X, page 350). If Hardy's experiments are correctly interpreted, wholly different intermolecular forces of microscopic range have to be recognized, as indeed they are by a number of investigators.

² Now more commonly termed homopolar. The internuclear distance is 1.26 Å., the dipole length 0.216 Å. (K. Fajans, *Z. Elektrochem.*, 1928, **34**, 503).

³ Some formed by coupled electrons, others by an ion attracting a dipole; see L. Pauling, *J. Am. Chem. Soc.*, 1931, **53**, 1367.

DEFINITION AND CHARACTERIZATION OF DIPOLES

Of electrostatic attractions there are only three sources; namely, free charged ions, permanent dipoles and temporary or induced dipoles or polarized molecules or atoms. The standard treatise upon the subject of dipoles is that of Debye¹ to which the reader is referred.

The theory and measurement is intimately connected with that of dielectric constants. The classical conception of dielectrics of Clausius-Mossotti appears to be reinstated in modern theory. If ϵ is the dielectric constant then

$\frac{\epsilon - 1}{\epsilon + 2}$ = the fraction of the volume actually occupied by the

molecules = $\frac{1}{4} b$ where b is the constant of van der Waals' equation. The molar polarization P which a medium ex-

periences in an electrostatic field may be set equal to $\frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d}$

where M is the molar weight and d the density. This expression includes effects due to dipoles and the polarization of ordinary molecules, and it is therefore necessary to define and consider these more closely. A dipole or permanent dipole is one in which the centres of gravity of the positive and negative charges do not coincide; for example, sulphur dioxide, water, or ammonia. Such molecules are equivalent to a proton and electron separated by a small distance l , their dipole moment μ being defined as

$$\mu = l \times \text{charge.}$$

Symmetrical molecules such as carbon dioxide, carbon tetrachloride, benzene and the paraffins possess no such permanent moment but are the equivalent of quadrupoles or other symmetrical arrangements of dipoles such as two identical dipoles

¹ P. Debye, *Polare Molekeln* (Hirzel, Leipzig, 1929); *Polar Molecules* (Chemical Catalog Co., Inc., New York, 1929). See also E. Hückel, *Adsorption und Kapillarkondensation*, p. 85 (Akademische Verlagsgesellschaft, m.b.H., Leipzig, 1928); O. Blüh and N. Stark, *Die Adsorption*, p. 40 (F. Vieweg und Sohn, Braunschweig, 1929); J. Estermann, *Ergebnisse der exakten Naturwissenschaften*, 1929, **8**, 258; C. P. Smyth, *Chem. Reviews*, 1929, **6**, 549; J. W. Williams, *Chem. Reviews*, 1929, **6**, 589; F. G. Keyes, *Chem. Reviews*, 1929, **6**, 175.

placed end to end with like charges together. So long as they remain symmetrical, that is, never during sorption, they are characterized by the three principal axes of the electrical moment of inertia. Dipoles are therefore represented by numbers of the order of 1×10^{-18} electrostatic units which, since one electronic charge equals 4.774×10^{-10} e.s.u., would correspond to a proton and electron 0.209 Å. apart. Quadrupoles are so defined that their numerical values appear as 1×10^{-24} e.s.u., which gives the impression of being of a lower order of magnitude.

An electrical field exerts the following influences on the three characteristic cases :

(a) On an ion—attraction.

(b) On a dipole—orientation plus attraction.

(c) On a symmetrical molecule or quadrupole—a deformation or polarization, the component charges being displaced in opposite directions, producing an induced dipole and therefore resulting in an attraction.

If the electrical field is alternating rapidly enough, as in the electromagnetic field of light waves, there is no time for the orientation of the whole molecule to take place, turning end for end with each wave, and therefore the effect would depend upon the frequency ν . Further, thermal vibration will interfere with perfect orientation, and the dielectric effect will accordingly have a temperature coefficient.

The deformation listed under (c) will, of course, likewise occur with permanent dipoles. Any two molecules or atoms when near each other will each undergo such displacement of positive and negative charges, such polarization, as to result in mutual attraction. This mutual attraction is similar to or often identified with van der Waals' forces. It may be recalled that the electrical fields in the neighbourhood of the atoms can be enormous. For example, the field at a distance of 1 Å. from an electron is 1.3×10^9 volts per centimetre. This would be sufficient¹ to induce a dipole of about 10^{-18} e.s.u., equal to most permanent dipoles.

The most interesting thing to remember in discussing polar

¹ O. Blüh and N. Stark, *Z. Physik*, 1927, **43**, 577.

and non-polar molecules is that they are singularly alike in their behaviour as regards sorption. The completely non-polar molecules, such as carbon dioxide, carbon tetrachloride, carbon disulphide, benzene, the saturated hydrocarbons and the rest, are as much sorbed as those with the highest permanent dipole moments. Reference to earlier chapters will illustrate this by the closely similar behaviour of carbon dioxide and ammonia, one non-polar and the other a strong dipole. There appears to be an unjustified impression in many quarters that, because the dipole moment is expressed in units of 10^{-18} e.s.u. and quadrupole moments in units of 10^{-24} e.s.u., the effects exhibited by the former must completely overshadow the influences due to the latter. That this is not necessarily the case is strikingly exhibited by the fact that Magnus from the data of sorption of carbon dioxide by charcoal derived the fictitious value 2×10^{-18} e.s.u. for the dipole moment of carbon dioxide. Exactly the same data in the hands of Blüh and Stark¹ led to the value 3.7×10^{-26} e.s.u. for the electric moment of inertia as a quadrupole, in agreement with Debye's value from van der Waals' forces of 3.9×10^{-26} e.s.u.

The molar polarization referred to above includes numerous effects.

$$P = P_{\mu} + P_{\text{electronic}} + P_{\text{atomic}} + P_{\text{ionic}} + P_{\text{radicals}} + P_{\text{proximity}} + P_{\text{association}} + \text{etc.}$$

Here P_{μ} represents the effect of the permanent dipole with its orientation polarization, diminishing with the thermal vibration of higher temperatures. $P_{\text{electronic}}$ is the "induced dipole" due to the electronic displacement which can follow even the rapidly alternating fields of visible light. The remaining terms are all distortions of larger units such as atoms in groups within the molecule or, as in the case of $P_{\text{proximity}}$, the effect of neighbouring molecules illustrated by viscosity in liquids. $P_{\text{association}}$ is illustrated in colloidal systems such as the glasses. All of these are described by

¹ N. Stark and O. Blüh, *Physik. Z.*, 1927, **28**, 502.

the words deformability or polarizability where sufficient time is available for such displacement to occur.

Most of these deformations are not always taken into account in the usual theoretical and experimental treatment of the subject of dipoles, although they are of proven importance in the subject of sorption and in the structure of non-crystalline matter. For example, protein molecules which the ultracentrifuge shows to be spherical in solution are spread out into single sheets, molecular chains or networks on the surface of mercury or upon the surface of acidified aqueous solution.

Considering only the first two terms, P_μ and $P_{\text{electronic}}$ or P_e , P is usually set equal to $\frac{\text{constant}_1}{T} + \text{constant}$. P_μ according to Debye, may be set equal to

$$P_\mu = \frac{4\pi N}{9} \frac{\mu^2}{kT}$$

where N is the Avogadro number, T the absolute temperature, and k the Boltzmann constant 1.372×10^{-16} . P_e according to the Lorentz-Lorenz formula is related to the index of refraction of light, extrapolated to infinite wave length.

$$P_e = \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \frac{M}{d} = MR_\infty.$$

$MR_\infty = \frac{4}{3}\pi a N$ where a is the polarization constant and the moment $= a X$ where X is the field strength.

It is evident from these considerations that the values of P_μ and P_e may be distinguished by the temperature coefficient of the dielectric constant. The two chief methods of measuring them are to observe the dielectric constant of the gas at various temperatures (not very accurate in practice) and to note the difference between dielectric constant and molar refraction MR_∞ in very dilute solution in an indifferent solvent so as to avoid mutual effects of the permanent dipoles for each other.

The application of the subject of dipoles to the calculation of the magnitude of the effects observed in sorption has not

yet proceeded very far. Keesom¹ ascribed sorption to the orientation of permanent dipoles but Debye takes the more general view that it is due to polarization or induced dipoles.

The mathematical treatment requires expressions for the potential of ions, dipoles and quadrupoles, first neglecting polarization and then obtaining expressions for the attractions of dipoles, quadrupoles and the attractive constant a of van der Waals' equation.² Lorenz and Landé have further considered the attractive forces which dipoles approaching a continuous surface call into being and which resemble those between a dipole and a mirror image of opposite sign. Finally, quadrupoles similarly mirrored have been considered.

ANALYSIS OF FORCES AT A CRYSTAL SURFACE

One of the clearest analyses of the various electrostatic forces available at a surface is that made by Lennard-Jones and Miss Dent³ for the (100) face of an ionic crystal of the type of sodium chloride where the available forces are exceptionally strong.

There are four forces to take into account⁴:

¹ W. H. Keesom, *Physik. Z.*, 1921, **22**, 129.

² The latter is closely connected with surface tension σ . The equation of Eötvös $\sigma^{\frac{1}{3}} = a(T_k - T)$ yields by experiment the constant $a = 2.1$. From the calculation of the attraction of dipoles the value 2.57 is obtained and from the calculations for quadrupoles 2.06.

³ J. E. Lennard-Jones and B. M. Dent, *Trans. Farad. Soc.*, 1928, **24**, 92, which see for the calculations, none of which are reproduced here. See also the similar considerations of O. Blüh and N. Stark, *Z. Physik*, 1927, **43**, 575.

⁴ A simple treatment is given by J. H. de Boer, *Proc. Acad. Sci. Amsterdam*, 1928, **31**, 906; *Physica*, 1928, **8**, 145. J. Gickhorn, R. Fürth and O. Blüh (*Z. physik. Chem.*, 1926, **123**, 359) believe that if one pole of a dipole is more nearly exposed than the other, it will be preferentially attracted to a body of opposite charge; they adduce experiments with oxygen and ammonia which may be examples of such behaviour. Otherwise, a charge on a solid, whether positive or negative, will always enhance adsorption. O. Blüh and N. Stark (*Z. Physik*, 1927, **43**, 581) estimate this increase as $\cosh \frac{\mu E}{kT}$ fold, where μ is the dipole moment and E the field. Thus for a field of

(1) Direct electrostatic attraction of any ion that may approach the crystal from the gaseous phase. This is, of course, of no practical importance from the standpoint of sorption except as a standard of comparison.

(2) The polarization of the sorbed molecule $P = P_e + (P_{etc.})$ due to the electrostatic field arising from the charge of the ions on the surface of the space lattice. The force required to remove to an infinite distance a permanent dipole of relatively large length from an initial distance of 3 Å. from the surface is about 7,000 calories per gram mol. This force (2) "is naturally very much less than the electrostatic force" (1), "and falls away much more rapidly".¹ When the distance of the molecule from the surface of sodium chloride, whose lattice spacing a is 5.63 Å., is increased from 2.81 Å. to 5.63 Å., this force is decreased 10,000 fold.

(3) $P = P_e + (P_{etc.})$ suffered by the ions of the lattice themselves, due to the reaction of (1) or (2). This is negligible except for (1).

(4) $P = P_e + (P_{etc.})$ of the sorbed molecule due to the structure of the ions of the space lattice as distinguished from their free ionic charges; that is, the van der Waals' or cohesional forces. These forces can be simulated by assuming a repulsion varying as one inverse power of the distance together with an attraction varying with a smaller inverse power of the distance. It was found necessary to assume that the repulsive power is 9, 10 or 11 and the attractive power 5 or possibly 6 or 7. The net attraction then falls off rapidly at first but finally varies only with the second power of the distance. They are the forces usually responsible for sorption where no free charges occur, either in solid or gas. The forces thus possible outside a crystal surface are pictured in fig. 148² and the corresponding potentials for two particular 1×10^5 volt/cm. the adsorption would be increased by one per cent, for 1×10^6 volts/cm. by 40 per cent, and for 1×10^9 volts/cm. by 10,000 per cent.

¹ J. E. Lennard-Jones and B. M. Dent, *Trans. Farad. Soc.*, 1928, **24**, 100.

² J. E. Lennard-Jones and B. M. Dent, *Trans. Farad. Soc.*, 1928, **24**, 105, fig. 1.

518 HYPOTHESES AND THEORY OF SORPTION

crystals, sodium fluoride and potassium chloride, are given in figs. 149 and 150.¹

It will be seen from the figures that the curves marked 1) are not of interest for our purpose; that the curves marked 3) are wholly negligible except at very short distances; indeed

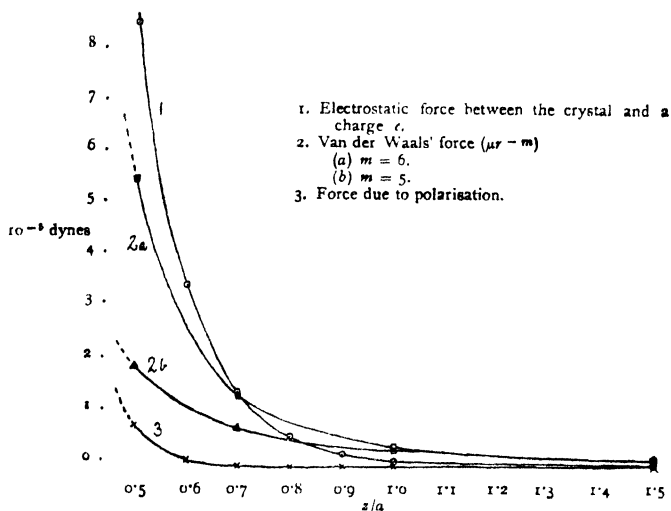


Fig. 148.—Electrostatic Forces outside the (100) Face of a Crystal acting upon 1) a Free Ion; 2) a Molecule or Atom through van der Waals' Forces assuming a Repulsive Force varying with the Sixth Power, 2A, and with the Fifth Power, 2B, respectively, corresponding to (4) in the text; and 3) the Force due to Polarization by the Charged Lattice, corresponding to (2) in the text. The Ordinates are dynes $\times 10^3$, the Abscissæ z/a , where z is the distance of the atom or molecule from the surface and a the lattice spacing.

in fig. 148 this curve falls below the base of the diagram and we are left with the van der Waals' forces which fall off with great rapidity but with a residual effect of longer range. The figures do not include the range where repulsion dominates. Many numerical values are tabulated in the original paper, where it is indicated "that the concentration of argon at the

¹ J. E. Lennard-Jones and B. M. Dent, *Trans. Farad. Soc.*, 1928, 24, 107 and 108, figs. 2 and 3.

distance of 10 Å. from KCl is about two or three times the normal at room temperature".¹ This is, of course, a mag-

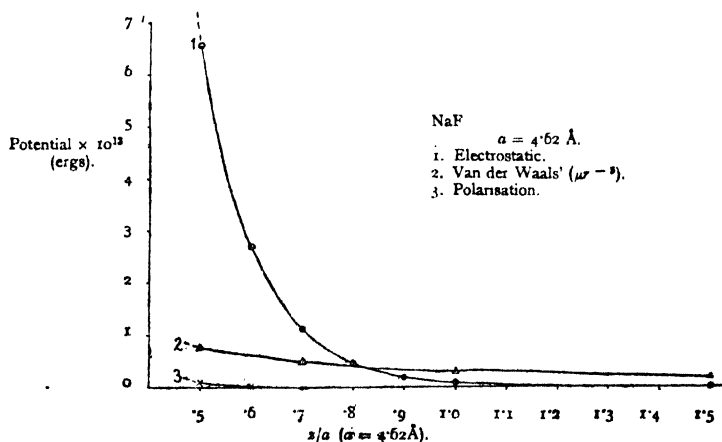


Fig. 149.—Potential in Ergs $\times 10^{-13}$ of Neon, charged and uncharged, outside a Crystal of Sodium Fluoride. The numbering of the curves and the explanations correspond to those in fig. 148 except that here it is assumed that the repulsive coefficient of the van der Waals' force is the fifth power.

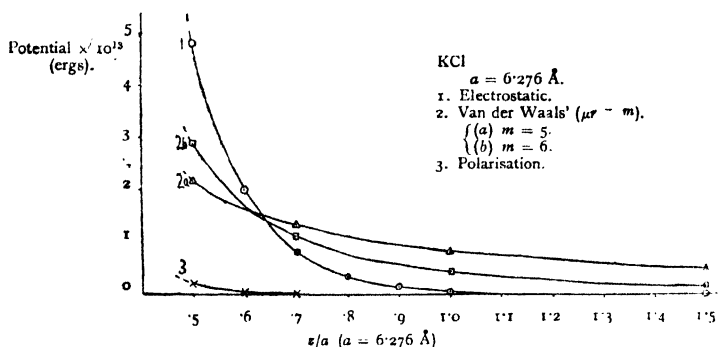


Fig. 150.—Potential in Ergs $\times 10^{-13}$ of Argon, charged and uncharged, outside a Crystal of Potassium Chloride. The numbering of the curves and the explanations correspond to those in fig. 148.

¹ J. E. Lennard-Jones and B. M. Dent, *Trans. Farad. Soc.*, 1928, 24, 107.

nitude far below that observed in measurements of sorption, as it would correspond to only a few thousandths of a monomolecular layer even at atmospheric pressure, and proportionally less at lower pressures.

We may therefore draw the conclusion from these numbers that these forces are of such small range that they are experimentally significant only for monomolecular sorption.

Masson,¹ discussing experiments on the compressibility of gaseous mixtures, points out that the van der Waals' forces are no greater between oxygen and ethylene than between argon and ethylene, and that

"a certain compressed mixture of argon with ethylene packed into a given volume under a pressure lower than it 'ought to be' by as much as 8.5 per cent." "Even in ordinary gaseous collisions the zone of maximum attraction was passed through and the repulsive region was entered; and this remained true though the atoms of the colliding molecules were of kinds that could combine together chemically."

Eucken² objected to explaining sorption as due to dipoles because this would demand an unduly large temperature coefficient. This objection, however, would apply chiefly to permanent dipoles. Lorenz and Landé³ took the view that the orienting force at the surface of the solid might be sufficiently great to offset thermal vibration to a large extent.

THE CONCEPT OF MIRRORED DIPOLES AND MIRRORED QUADRUPOLES

Many writers⁴ have availed themselves for purposes of calculation of a simplified conception. The solid is regarded

¹ I. Masson, *Trans. Farad. Soc.*, 1928, **24**, 168; I. Masson and L. G. F. Dolley, *Proc. Roy. Soc. (London)*, A, 1923, **103**, 524.

² A. Eucken, *Z. Elektrochem.*, 1922, **28**, 11.

³ R. Lorenz and A. Landé, *Z. anorg. allgem. Chem.*, 1922, **125**, 47.

⁴ P. Debye, *Physica*, 1921, **1**, 362; R. Lorenz and A. Landé, *Z. anorg. allgem. Chem.*, 1922, **125**, 54; I. Langmuir and K. H. Kingdon, *Proc. Roy. Soc. (London)*, A, 1925, **107**, 61; I. Langmuir and D. S. Villars, *J. Am. Chem. Soc.*, 1931, **53**, 486; E. Jaquet, "Theorie der Adsorption von Gasen," *Fortschritte Chem., Physik, physik. Chem.*,

as continuous and conducting. A dipole approaching such a surface will be attracted by it just as if the surface were a mathematical plane midway between the dipole and its mirror image with poles reversed. This is shown diagrammatically in fig. 151.

The dipole of length l and charge e possesses a dipole moment $\mu = l \cdot e$. If it is at a distance x from the surface, the distance between the centres P and P' is $h = 2x$. Were it not for thermal vibration the dipole would remain perpendicular to the surface. As it is, at a particular moment it may be at an angle θ to the perpendicular.

The potential at the middle of the dipole P will be

$$\varphi^1 = \frac{\mu}{h^3} \cdot \cos \theta.$$

Debye's expression for the potential energy of the dipole and its mirror image is

$$\varphi = -\frac{\mu^2}{h^3} \cdot (1 + \cos^2 \theta).$$

The energy of adsorption is therefore proportional to the square of the dipole moment or proportional to the van der

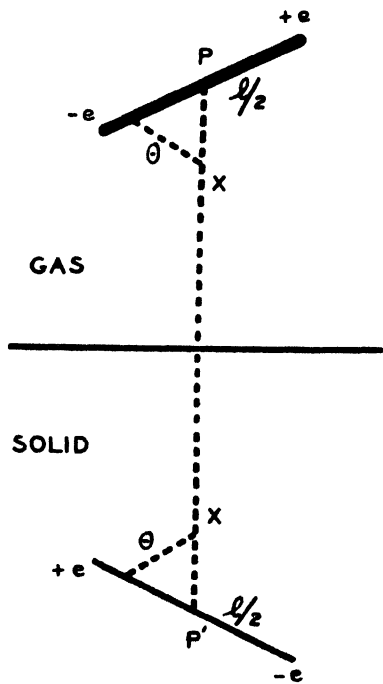


Fig. 151.—Diagram of a Dipole attracted by its Fictive Mirror Image (with poles reversed).

Series B, 1925, **18**, Heft 7, p. 19; A. Magnus and H. Roth, *Z. anorg. allgem. Chem.*, 1926, **150**, 311; A. Magnus and M. Braner, *Z. anorg. allgem. Chem.*, 1926, **151**, 150; A. Magnus, *Z. anorg. allgem. Chem.*, 1926, **158**, 67; *Z. physik. Chem.*, Abt. A, 1929, **142**, 401 (Magnus' complete theory); *Z. Elektrochem.*, 1928, **34**, 531.

Waals' constant a . Blüh and Stark¹ point out that for a dipole of moment about 10^{-18} e.s.u. and a value for h of about 10^{-8} , this gives a value per molecule of about 10^{-12} ergs. This is a reasonable value, for it corresponds with an adsorption potential for one gram mol equal to 15,000 calories.

If c_∞ is the concentration in the uniform gaseous atmosphere at a distance from the solid, and c_x is the concentration at the point illustrated in fig. 151 at a distance x from the surface,

$$c_x = c_\infty \frac{e^{2y}}{2y} \text{ where } y = \frac{\mu^2}{h^3 k T} > 1.$$

This equation shows that the concentration falls off with extreme rapidity with increase of x in the neighbourhood of the surface; hence such adsorption must be essentially monomolecular.

The amount sorbed, in mols per square centimetre, A , is

$$A = \int_{x_0}^{\infty} (c_x - c_\infty) dx = \frac{p_\infty x_0 e^{\frac{C}{T}}}{3RC \cdot \frac{C}{T}}$$

where x_0 is the nearest approach to the surface, and where the gas is assumed perfect, and where C is a term introduced by Lorenz and Landé² with the dimensions of a temperature

$$C = \frac{\mu^2}{4x_0^3 k}.$$

The heat of sorption q is approximately

$$q = RC - RT$$

and it would therefore be zero at the temperature indicated by C , which is called the characteristic or critical temperature of adsorption.

It is evident that the dipole moment could be calculated from C if x_0 (and the surface) were known with sufficient accuracy

$$\mu = \sqrt{2kx_0 C}.$$

¹ O. Blüh and N. Stark, *Die Adsorption*, Sammlung Vieweg, Heft 93 (Vieweg und Sohn, Braunschweig, 1929).

² R. Lorenz and A. Landé, *Z. anorg. allgem. Chem.*, 1922, **125**, 51.

Jaquet extended the above treatment significantly by estimating how much greater the potential energy would be if the permanent dipole were also to become polarized, a further dipole moment to be induced. He found that at very low temperatures the energy would be increased by one-third, but this would rapidly diminish with increase of temperature.

The fact is, however, that molecules which have no permanent dipole moment are freely sorbed even by metals. Palmer¹ found the Lorenz and Landé formulation so successful with dipolar molecules as studied by the coherer method that he extended its application equally to non-polar molecules. He made the novel suggestion in justification that molecules colliding in the gas phase near the surface of the solid are distorted and may be temporarily powerful dipoles and therefore be held to the surface in this activated state. Since collisions increase with rising temperature, this activated adsorption might also so increase (compare Chapter III, page 45; also this chapter, next subsection²). A symmetrical molecule with no permanent dipole moment is generally characterized by the electrical moment of inertia τ , where τ is of the order of $10\frac{1}{2} \times 10^{-26}$ e.s.u. For a molecule constructed like two dipoles laid end to end $\tau = 2el^2$. If such a rod-shaped quadrupole is mirrored in a surface, the energy of the quadrupole and its mirror image is given by Jaquet as

$$\varphi = -\frac{9}{128} \frac{\tau^2}{x^5} (1 + \frac{3}{2} \cos^2 \theta + \cos^4 \theta).$$

Further,

$$c_x = c_\infty \int_0^1 e^{-\frac{\phi}{kT}} d \cos \theta.$$

As a first approximation,

$$c = c_\infty \cdot \frac{1}{2\sqrt{6}} \cdot \frac{e^{y(1+\sqrt{8/3})}}{y}.$$

¹ W. G. Palmer, *Proc. Roy. Soc. (London)*, A, 1927, **115**, 234.

² For other suggestions as to modes of polarization of adsorbed molecules, see Chapter XIX and references given by H. S. Taylor, *Proc. Roy. Soc. (London)*, A, 1926, **113**, 78.

The adsorption is, in mols per square centimetre,

$$A = \frac{c_{\infty} x_0}{10\sqrt{6}} \cdot \frac{e^{2.6\frac{C}{T}}}{\left(2.6\frac{C}{T}\right)^2}.$$

$$\text{where} \quad C = \frac{9\tau^2}{128kx_0^5}.$$

The heat of sorption q is approximately

$$q = 2.6RC - RT.$$

Hence a knowledge of heat of sorption yields a value for C ; and a further exact knowledge of x_0 would give the value of τ

$$\tau = \frac{8}{3}\sqrt{2kx_0^5C}.$$

It requires no emphasis that the idealized conditions here discussed must usually be remote from reality. It is assumed that the solid is fine grained in comparison with the size of the molecule adsorbed, that the surface is smooth and conducting, and that attractive centres are not localized as are primary or residual valencies of particular surface atoms, or the special points of attraction such as corners or other spatial arrangements.

In the next place, a single molecule of gas is contemplated, remote from neighbours and approaching the surface in its normal condition, not distorted or polarized by recent collision, which would seriously affect the assumptions made. Finally, it is assumed that even upon the surface it is remote from its neighbours. Hence comparison with actual data is confined to the region where Henry's law appears to apply.¹ That this must often be illusory and merely due to the actual presence of extraneous molecules and impurities on the surface is illustrated by the experience of the writer and others with progressively cleaned surfaces. See, for example, Chapter IV, pages 92, 128 and 129, Chapter IX, page 321, etc.

¹ When the values of C obtained by comparison of isotherms at various temperatures do not yield a constant, it is concluded that Henry's law could not have applied but was simulated by experimental error. See for example, A. Magnus and H. Roth, *Z. anorg. allgem. Chem.*, 1926, **150**, 324.

MUTUAL POLARIZATION OF SORBED MOLECULES

Mutual proximity may greatly stabilize sorbed molecules, even in activated form.¹ This is illustrated by the thermionic properties of barium adsorbed on tungsten, where the proportion of ionized atoms increases with increase in covering of the surface.² It is most strikingly exemplified by the sorption of water upon drastically evacuated charcoal as studied by the writer and Dr. Sessions³ where the water is not very appreciably sorbed below a relative pressure of 0.3 but at this pressure almost the full amount is sorbed.

Herzfeld⁴ discusses in detail the mutual polarization of sorbed molecules.

“ This polarization of the molecules will set up much stronger forces between them than in the absence of an external field, in the same way in which two rods of soft iron which do not attract each other appreciably outside of an external magnetic field act on each other strongly if magnetized by an outside source.” “ In this case the interaction can be much stronger than the usual heat of evaporation would lead us to expect.”

Herzfeld considers both attractions and repulsions between adsorbed molecules in various cases and shows how sometimes the heat of sorption may increase with increasing amount of sorption, concluding that in such cases groups of molecules sticking together are formed.

Mutual polarization is doubtless the reason for the formation of two-dimensional liquids from two-dimensional vapours.⁵ Magnus⁶ and Hückel⁷ considered dipoles oriented in the same

¹ Compare W. G. Palmer, *Proc. Roy. Soc. (London)*, A, 1927, **115**, 234; this chapter, page 523.

² J. A. Becker, *Phys. Rev.*, (2), 1929, **33**, 1082.

³ Chapter IV, page 148.

⁴ K. F. Herzfeld, *J. Am. Chem. Soc.*, 1929, **51**, 2609. See also A. Magnus, *Z. Elektrochem.*, 1928, **34**, 531.

⁵ For a discussion of mutual polarization in general (solutions, vapours, crystal lattices, etc.) see K. Fajans, *Z. Elektrochem.*, 1928, **34**, 503; H. F. Hertlein, *Ann. der Physik*, (5), 1930, **4**, 898; B. Tamamushi, *J. Chem. Soc. Japan*, 1930, **51**, 166.

⁶ A. Magnus, *Z. physik. Chem.*, Abt. A, 1929, **142**, 423.

⁷ E. Hückel, *Adsorption und Kapillarkondensation*, p. 193 (Akademische Verlagsgesellschaft, Leipzig, 1928).

direction and repelling each other, therefore emphasizing the equation

$$\left(\pi - \frac{\alpha}{\Omega^2}\right)(\Omega - \beta) = RT$$

in analogy with van der Waals' equation, but with a negative sign ¹ for α .

OTHER DIELECTRIC RELATIONS

Keyes and Marshall ² in their studies of heat of sorption of gases and vapours on charcoal found a direct parallelism between final heats of sorption (less external work) and the dielectric properties of the gas as observed directly or as evinced in the constants of the equation of state.

Iliin's discussions ³ attempt to relate the dielectric constant ϵ of the gas, the "adsorption-capacity", the heat of sorption, and the assumed lowering of surface tension of the solid, using for the latter analogies with the surface tensions of aqueous solutions. For the dipole moment μ he sets

$$\mu = \frac{\sigma_0}{4\pi k} \left(\frac{\epsilon - 1}{\epsilon} \right)$$

where σ_0 is the surface tension of the solid in a vacuum and k the Boltzmann constant. The heat of sorption q is set equal to

$$q = (\sigma_0 - \sigma_1)\Omega$$

where σ_1 is the lowered surface tension resulting from sorption of the gas. For this he has been severely criticized by Cassel ⁴ who points out that the second law of thermodynamics requires a term for the temperature coefficient of the lowering of

¹ Compare B. Tamamushi, *Bull. Chem. Soc. Japan*, 1927, **2**, 299; 1928, **3**, 142.

² F. G. Keyes and M. J. Marshall, *J. Am. Chem. Soc.*, 1927, **49**, 170.

³ B. Iliin, *Z. physik. Chem.*, 1923, **107**, 145; *Phil. Mag.*, (6), 1924, **48**, 193; *J. Russ. Phys. Chem. Soc.*, Physical Part, 1924, **56**, 2; *Phil. Mag.*, (6), 1925, **50**, 1144; *Physik. Z.*, 1925, **26**, 497; *Z. Physik*, 1925, **33**, 435; *Z. physik. Chem.*, 1925, **116**, 431; *Physik. Z.*, 1926, **27**, 591; W. Tarassoff, *Physik. Z.*, 1924, **25**, 369.

⁴ H. Cassel, *Physik. Z.*, 1925, **26**, 862; 1927, **28**, 152.

surface tension, neglect of which may introduce an error of as much as ten-fold in Iliin's calculations. The best comparison of existing data with Iliin's equation is given by Gregg ¹ who found it necessary to introduce empirical correcting terms for nine gases examined, but even so did not find agreement for sulphur dioxide and ammonia sorbed by charcoal.

Kar and Ganguli ² studied polar adsorption statistically and found no fundamental difference between electrical and chemical adsorption. Their expression, like those of so many other workers approaching the subject of sorption by different methods, and from different points of view, is like that of Langmuir.

¹ S. J. Gregg, *J. Chem. Soc.*, **1927**, 1510.

² K. C. Kar and A. Ganguli, *Z. Physik*, 1930, **61**, 411.

AUTHOR INDEX

- Aborn, R. H., and Davidson, R. L. 360
- Abrams, A., and Chilson, W. A. 371
- Adam, N. K. 472
- Adams, A. S. 231
- Adams, E. Q. (see *Bohart, G. S.*)
- Adhikari, G. (see *Volmer, M.*)
- Adhikari, G., and Felman, J. 327
- Adkins, H. (see *Bischoff, F.; Lazier, W. A.*)
- Adkins, H., and Lazier, W. A. 489
- Adkins, H., and Nissen, B. H. 489
- Adler, R. 66
- Aharoni, J. 23 (see *Simon, F.*)
- Aharoni, J., and Simon, F. 174, 298, 301
- Akim, L. (see *Hess, K.*)
- Alekseevski, E. V. 25, 52, 138, 200, 385, 425
- Alexander, J., and McBain, J. W. 71
- Alexejew, D., and Matalski, V. 386
- Alexeyevskii, E. V. (see *Alekseevski*)
- Alleman, G., and Darlington, C. J. 260
- Allen, E. T., and Zies, E. G. 223
- Allen, H. S. (see *Blythswood, Lord*)
- Allen, W. S. (see *Porritt, B. D.*)
- Allmand, A. J. 152
- Allmand, A. J., and Burrage, L. J. 25, 40, 469
- Allmand, A. J., and Chaplin, R. 70, 132, 152, 164, 408
- Allmand, A. J., Chaplin, R., and Shiels, D. O. 52, 70, 144, 150, 151
- Allmand, A. J., and Hand, P. G. T. 52, 70, 144, 150, 151
- Allmand, A. J., Hand, P. G. T., and Manning, J. E. 144, 150, 152, 153
- Allmand, A. J., Hand, P. G. T., Manning, J. E., and Shiels, D. O. 144, 150, 151
- Allmand, A. J., and King, R. B. 150
- Allmand, A. J., and Manning, J. E. 25, 132
- Allmand, A. J., and Puttick, A. 94, 132
- Allolio, R. (see *Bredig, A.*)
- Almquist, J. A., and Bray, W. C. 210, 500
- Altmayer, V. (see *Mayer, M.*)
- Alvarado, A. M. (see *Pearce, J. N.*)
- Amagat, E. H. 461
- Amberger, C. (see *Paal, C.*)
- Anderson, J. A. (see *Holmes, H. N.*)
- Anderson, J. S. 146, 187, 188, 434
- Anderson, P. 267
- Andress, K. (see *Berl, E.*)
- Andress, K., and Berl, E. 425
- Andress, K. R. 360, 362
- Andrew, G. W. (see *Bone, W. A.*)
- Andrew, J. H. 298, 396
- Andrew, J. H., and Holt, A. 298
- Andrews 500
- Andrews, D. H., and Johnston, J. 385
- Andrews, D. H., Witt, R. K., and Crigler, E. 400
- Andrews, R., and Bacon, J. S. 218
- von Antropoff, A. 157
- Applebey, M. P. (see *Ferguson, J.*)

- Appleyard, J. R. (see *Walker, J.*)
 Armstrong, E. F., and Hilditch, T. P. 499, 503, 505
 Armstrong, H. E. 123
 Aronstein and Sirks 386
 Arrhenius, S. 54, 95
 Asahara, G. 67
 Astbury, W. T., and Street, A. 377
 Astbury, W. T., and Woods, H. J. 377, 382
 Åström, A. 358
 Aubel, E. (see *Devaux, H.*)
 Auerwald, C. (see *Paal, C.*)
 Austerweil, G. 386

 Baba, T. 174
 Bachmann, W. 153, 177, 187, 191, 192, 395, 441, 442 (see *Zsigmondy, R.*)
 Bachmann, W., and Maier, L. 184
 Backe, H. (see *Ruff, O.*)
 Bacon, J. S. (see *Andrews, R.*)
 Baerwald, H. 65, 86, 93, 103, 111, 135, 289, 290
 Baker, C. J. 9
 Baker, H. B. 9, 169, 214 (see *Winter, R. M.*)
 Bakr, A. M. 372 (see *McBain, J. W.*)
 Bakr, A. M., and King, J. E. 24, 128, 162, 165
 Bakr, A. M., and McBain, J. W. 128, 140, 372
 Balandin, A. A. 489, 509
 Bancelin, J. 328, 337, 339
 Bancroft, W. D. 182, 217, 499
 Bancroft, W. D., and Barnett, C. E. 118, 336, 383
 Bangham, D. H. 392
 Bangham, D. H., and Burt, F. P. 47, 48, 241
 Bangham, D. H., and Fakhoury, N. 391, 439
 Bangham, D. H., and Sever, W. 48, 236
 Bangham, D. H. and Stafford, J. 48, 71, 440
 Bannister, L. C. (see *Evans, U. R.*)
 Barclay, E. H. (see *Patrick, W. A.*)
 Barcroft, J. 472
 Barker, J., and Priestley, L. P. 380, 382, 384
 Barker, M. E. 67, 68, 70, 72, 78, 84, 86
 Barker, S. G. 379, 380, 382
 Barker, S. G., and Hedges, J. J. 378, 380
 Barnett, C. E. (see *Bancroft, W. D.*)
 Barr, G. 386 (see *Rosenhain W.*)
 Barr, G., and Thomas, J. 386
 Barritt, J., and King, A. T. 380
 Barry (see *Flusin*)
 Bartell, F. E., and Fu, Y. 344, 346, 425
 Bartell, F. E., and Osterhof, H. J. 149, 345, 447
 Barth, W. (see *Hock, L.*)
 Bartsch, O. 496
 Bary, P. 385
 Bary, P., and Hauser, E. A. 384
 Baudisch, O. (see *Welo, L. A.*)
 Baule, B. 465
 Baumgarten, H. (see *Cohn, A.*)
 Baxter, G. P. 309, 310
 Bay (see *Vignon*)
 Bayliss, W. M. 472, 481
 Beattie, J. A., and Bridgeman, O. C. 488
 Becker 399
 Becker, E. (see *Schwalbe, C. G.*)
 Becker, J. A. 473, 525
 Beebe, R. A., and Taylor, H. S. 421
 Bellati, M. 424
 Bellati, M., and Finazzi, F. 424
 van Bemmelen, J. M. 5, 159, 181, 182, 183, 185, 191, 192, 193, 365, 395, 441, 473, 481
 Bennett, H. B. (see *Jenkins, W. J.*)
 Bennewitz, K. 465

- Benton, A. F. 209, 279, 280, 281, 282, 284 (see *Markham, E. C.*)
 Benton, A. F., and Elgin, J. C. 265
 Benton, A. F., and White, T. A. 312, 313, 314
 Berend, G. (see *Pietsch, E.*)
 Berényi, L. 450, 452, 454, 455, 458, 473, 477, 478
 Bergner, E. (see *Sieverts, A.*)
 Bergter, F. 48, 160, 164
 Berl, E. (see *Andress, K.*)
 Berl, E., and Andress, K. 86, 130, 134, 144, 150, 159, 452
 Berl, E., and Burkhardt, H. 181, 193
 Berl, E., and Schmidt, O. 161
 Berl, E., and Wachendorff, E. 134, 200
 Berliner, A. 264, 277, 281, 289, 394
 Bernays, P. 166
 Berry, A. J. 288
 Berthelot 282
 Berthelot, D. 458
 Berthelot, M. 123
 Berthelot, M., and Guntz, A. 120
 Bertrand, A. (see *Jamin, A.*)
 Berzelius 498
 Bewilogua, L. (see *Debye, P.*)
 Bhatia, S. L. (see *Bhatnagar, S. S.*)
 Bhatnagar, S. S., and Bhatia, S. L. 54
 Biewend, E. 53
 Biggs, H. F. 300
 Biltz, K. 371
 Biltz, M. 203 (see *Hahn, O.*)
 Biltz, W. 168, 233
 Biltz, W., and Fetkenheuer, B. 168
 Biltz, W., and Hüttig, G. F. 168
 Biltz, W., and Rahlfs, E. 172, 186, 197
 Bing, K. (see *Katz, J. R.*)
 Birutowitsch, St. (see *Traube, J.*)
 Bischoff, F., and Adkins, H. 204, 489
 Bjercke, A. (see *Freundlich, H.*)
 Blake, J. T. (see *Boggs, C. R.*)
 Blench, E. A., and Garner, W. E. 10, 404, 419
 Blinoff, G. (see *Kautsky, H.*)
 Blodgett, K. (see *Lemon, H. B.*)
 Blüh, O. (see *Gicklhorn, J.*; *Simon, F.*; *Stark, N.*)
 Blüh, O., and Stark, N. 327, 512, 513, 516, 522
 Blythswood, Lord, and Allen, H. S. 51
 Bochow, K. (see *Tammann, G.*)
 Bodenstein, M. 355, 498, 500
 Bodenstein, M., and Fink, C. G. 356, 498, 499
 Boedecker, C. 5
 Boehm, J. 9, 377
 de Boer, J. H. 258, 285, 496, 516
 de Boer, J. H., and Zwikker, C. 327, 496
 Boggs, C. R. (see *Wiegand, W. B.*)
 Boggs, C. R., and Blake, J. T. 385
 Bohart, G. S., and Adams, E. Q. 25, 120
 Boija, J. 371
 du Bois-Reymond, E. 7
 Bone, W. A. 500
 Bone, W. A., and Andrew, G. W. 500, 506
 Bonhoeffer, K. F., and Farkas, L. 235
 Bonhoeffer, K. F., and Harteck, P. 270
 Booth, H. (see *Rosenhain, W.*)
 Borelius, G. (see *Linde, J. O.*)
 Bose, E. 259, 266
 Bosshard, E., and Jaag, E. 179, 194, 393, 394, 413
 Boswell, M. C., and McLaughlin, R. R. 280, 282
 Bowden, F. P. 340, 341
 Bowden, F. P., and O'Connor, E. A. 340, 342
 Bowden, F. P., and Rideal, E. K. 340
 Boyle, R. W. 159

- Bozorth, R. M. (see *Lowry, H. H.*)
 Bradley, R. S. 488
 Bragg, W. (see *Eccles, W. H.*)
 Bragg, W. H. 360
 Bragg, W. L. 168
 Bramston-Cook, H. E. (see *Marshall, M. J.*)
 Braner, M. (see *Magnus, A.*)
 Bräuer, A., and Reitstötter, J. 58
 Bray, W. C. (see *Almqvist, J. A.*; *Hoskins, W. M.*)
 Bray, W. C., and Doss, G. J. 500
 Bray, W. C., and Draper, H. D. 210, 373, 441, 442
 Bredig, A., and Alolio, R. 302
 Brefeld, W. (see *Warburg, A.*)
 Breithaupt 179
 Brender à Brandis, G. A. 66
 Brewster 181
 Bridgeman, O. C. (see *Beattie, J. A.*)
 Bridgman, P. W. 53
 Briggs, H. 69, 78, 86, 87, 177, 179, 193
 Briggs, H., and Cooper, W. 108
 Briggs, L. J. 247, 248
 Brimley, R. C. 369
 Britton, G. T. 430, 440; (see *McBain, J. W.*)
 Brodie, B. C. 123
 Brown, B. E. 144
 Brown, W. E. L. 472
 Brückner, H. 508
 Brüninghaus, L. 350
 Brunswig, H. 362, 371
 Bryant, E. G. 380
 Buckingham, R. 372
 Bull, H. I., and Garner, W. E. 404, 417, 418
 Bülmann, E., and Klit, A. 292
 Bunbury, H. M. 141
 Bunsen, R. W. 219, 221, 224, 238, 239, 447, 449
 Bunting, E. N. (see *Washburn, E. W.*)
 Burdon, R. S. (see *Oliphant, M. L.*)
 Burk, R. E. 488, 499, 509
 Burk, R. E., and Gillespie, D. C. 489
 Burkhardt, H. (see *Berl, E.*)
 Burlet, E. 371, 380
 Burns, R. M. (see *Taylor, H. S.*)
 Burns, R. M., and Hulett, G. A. 71
 Burrage, L. J. 25, 132, 144; (see *Allmand, A. J.*)
 Burrgraff, A. J. (see *Klosky, S.*)
 Burstin, H., and Winkler, J. 406
 Burt, F. P. (see *Bangham, D. H.*; *Francis, M.*)
 Bush, V., and Connell, L. H. 219
 von Buzágh, A. 232
 Cagniard-Latour 386
 Cahn, L. (see *Magnus, A.*)
 Calvert, F. C. 9
 Cambi, L., and Szegoe, L. 196
 Cameron, H. K. 404, 407, 418
 Campbell, J. H. P. (see *Whytlaw-Gray, R.*)
 Carnelley, T., and Walker, J. 209
 Carr, A. R. (see *Leslie, E. H.*)
 Carr, A. R., and Murphy, D. W. 22
 Carver, E. K. 229, 234
 Cary, A., and Rideal, E. K. 355
 Cassel, H. 355, 356, 526
 Cazeneuve, P. 3
 Chakravarti, M. N., and Dhar, N. R. 330, 493
 Chamdler, C. de F. 386
 Chaney, N. K. 66, 67, 80, 91; (see *Lamb, A. B.*)
 Chaney, N. K., Ray, A. B., and St. John, A. 66, 67, 78, 91, 146, 178, 179
 Chaplin, R. 38, 93, 132; (see *Allmand, A. J.*)
 Chapman, P. F. (see *McBain, J. W.*)
 Chappuis, P. 114, 115, 240, 385, 405, 407, 408, 447, 491

- Chariton, J., and Semenoff, N. 149,
465, 483
 Chattock, 402
 Chilikin, M. M. 424
 Chilson, W. A. (see *Abrams, A.*)
 Chmutov, K. (see *Shilov, N.*)
 Chorazy, M. (see *Swientoslowski, W.*)
 Chowdhury, J. K., and Pal, M. N.
204
 Chufarov, G. I. 60, 62
 Clark, A. M. (see *Lambert, B.*)
 Clark, G. L. 67
 Claude, G. 157
 Clemente, A. 38, 141
 Coehn, A. 295
 Coehn, A., and Baumgarten, H.
292
 Coles, G., and Graham, J. I. 122
 Connell, L. H. (see *Bush, V.*)
 Constable, F. H. 342, 343, 506
 Coolidge, A. S. 18, 21, 28, 39, 94,
117, 118, 119, 125, 126, 130, 131,
132, 133, 135, 137, 138, 139, 141,
144, 145, 146, 147, 152, 155, 156,
401, 415, 416, 437, 438, 461;
(see *Lamb, A. B.*)
 Cooper, W. (see *Briggs, H.*)
 Copeland, P. L. 323, 350
 Costa, D. 377
 Coward, H. F., and Spencer, L. 371
 Coward, H. F., Spencer, L., and
Wood, F. C. 371
 Craig, G. 93
 Craik, J. (see *Miles, F. D.*)
 Crawford, J. G. 371
 Crespi, M. 242, 246; (see *Moles, E.*)
 Crespi, M., and Moles, E. 48, 242
 Crigler, E. (see *Andrews, D. H.*)
 Cude, H. E., and Hulett, G. A. 46,
88, 90, 139
 Curry, J. R. 234
 Czukor, K. 307
 Dankoff, R. 506
 Darby, E. H. (see *Kraus, C. A.*)
 Darlington, C. J. (see *Alleman, G.*)
 D'Arsonval 385
 Davey, W. C., and Ohya, T. 386
 Davidheiser, L. Y., and Patrick,
W. A. 197
 Davidson, G. F., and Shorter,
S. A. 371
 Davidson, R. L. (see *Aborn, R. H.*)
 Davies, D. P. 372, 373, 374
 Davies, G. P. (see *McBain, J. W.*)
 Davis, C. W., and Vacher, H. C.
393
 Davis, P. B. (see *Patrick, W. A.*)
 Davisson, C. J., and Germer, L. H.
322, 323, 487, 497
 Day, J. 248
 Day, J. E. 70
 Daynes, H. A. 386 (see *Shakes-
pear, G. A.*)
 Daynes, H. A., and Shakespear,
G. A. 28
 Debye, P. 489, 512, 514, 515, 516,
520, 521
 Debye, P., Bewilogua, L., and
Ehrhardt, F. 82
 Debye, P., and Scherrer, P. 67
 Degen, F. 53
 Deisenhammer, E. 71, 73
 Deming, W. E. 263
 Deming, H. G., and Hendricks,
B. C. 263
 Dent, B. M. (see *Lennard-Jones, J. E.*)
 De Prat, D. 386
 Devaux, H., and Aubel, E. 328
 Dew, W. A. 507
 Dew, W. A., and Taylor, H. S. 316,
422
 Dewar, J. 1, 9, 10, 37, 38, 42, 43,
47, 83, 95, 107, 108, 135, 157,
161, 162, 288, 290, 292, 300, 386,
397, 402, 403, 406, 419, 449; (see
Tait, P. G.)

Damianovich, H. 283

Damour, A. 167

- Dhar, N. R. (see *Chakravarti, M. N.*)
 Diekmann, H. (see *Tammann, G.*)
 Dietl, A. 51
 Ditmar, R. 385
 Dixon, J. K. 417; (see *Foote, H. W.*)
 Don Dobeneck, A. 247
 Döbereiner, 278
 Dobretsberger, H. 399
 Doelter, C. 167
 Doherty, W. H. 380
 Dolley, L. G. F. (see *Masson, I.*)
 Donnelly, R. P., and Hinshelwood, C. N. 506
 Dore, W. H. (see *Sponsler, O. L.*)
 Doss, G. J. (see *Bray, W. C.*)
 Dossmann, H. (see *Hartmann, C. A.*)
 Drane, H. D. H. 22
 Draper, H. D. 210, 441; (see *Bray, W. C.*)
 Driver, J., and Firth, J. B. 52, 64, 139, 144, 162
 Drucker, C. 233, 351
 Drucker, C., and Marxen, J. 233
 Drude, P. 26, 253
 Dubinin, M. (see *Shilov, N.*)
 Dubinin, M. M. 61
 DuBois, R. (see *McBain, J. W.*)
 Dubosc, A. 384, 385
 Duclaux, J. 509
 Dühring, U. 22
 van Duin, C. F. (see *Kruyt, H. R.*)
 Dumas 317
 Dunkel, M., and Mark, H. 493
 Dunnill, S. (see *Philip, J. C.*)
 Dupouy, J. R. 509
 Durau, F. 240, 241, 254, 255, 256, 257, 263, 265, 329, 331, 336; (see *Schmidt, G. C.*)
 Durocher (see *Malagutti*)
 Dushman, S. 215, 218, 259, 269, 331
 Dyer, J. W. W. 386
 Eberman, N. F. (see *Patrick, W. A.*)
 Eccles, W. H., and Bragg, W. 360
 Eckersall, N. (see *Urquhart, A. R.*)
 Eckling, K., and Kratky, O. 360
 Edgar, E. C. (see *Holt, A.*)
 Edser, E. 349
 Edwards, J. D. 386
 Edwards, J. D., and Pickering, S. F. 386
 Eggert, J., and Luft, F. 360
 Ehrenberg, P., and Schultze, K. 144
 Ehrhardt, F. (see *Debye, P.*)
 Eitel, W. 167
 Eitel, W., Herlinger, E., and Trömel, G. 395
 Elgin, J. C. (see *Benton, A. F.*)
 Ellerbroek, J. 26, 271, 272
 Elsdon, A. V. 213
 Emmett, P. H., and Love, K. S. 202
 Erbacher, O. (see *Willstätter, R.*)
 Essin, O. 356
 Estermann, J. 44, 353, 483, 512; (see *Volmer, M.*)
 Estermann, J., and Stern, O. 353
 Eucken, A. 55, 56, 346, 424, 430, 450, 458, 459, 489, 520
 von Euler, H. 331, 332, 481
 von Euler, H., and Hedelius, A. H. 332
 von Euler, H., and Rudberg, E. G. 332, 333
 von Euler, H., and Zimmerlund, G. 331, 332
 Evans, M. H., and George, H. J. 236
 Evans, U. R. 342
 Evans, U. R., and Bannister, L. C. 171, 342, 343
 Evans, U. R., and Stockdale, J. 342
 Ewing, D. T. (see *Harkins, W. D.*)
 Ewing, W. W. 411

- Ewles, J., and Speakman, J. B. 377
 Eyring, H., and Polányi, M. 471
- Fajans, K. 511, 525
 Fajans, K., and Frankenburger, W. 330
 Fakhoury, N. (see *Bangham, D. H.*)
 Faraday, M. 53, 212, 222, 498, 501
 Farkas, L. (see *Bonhoeffer, K. F.*)
 Farrow, F. D., and Swan, E. 376
 Favre, P. A. 60, 296, 407
 Favre, P. A., and Silbermann, J. T. 407
 Feige, F. (see *Ruff, O.*)
 Feigl, F. 121
 Fells, H. A., and Firth, J. B. 181
 Felman, J. (see *Adhikari, G.*)
 Felsing, W. A. (see *Keyes, F. G.*)
 Ferguson, I. (see *Schumacher, E. E.*)
 Ferguson, J. (see *McBain, J. W.*)
 Ferguson, J., and Applebey, M. P. 186
 Ferguson, J. B. (see *Rebbeck, J. W.*; *Williams, G. A.*)
 Fetkenheuer, B. 66; (see *Biltz, W.*)
 Field, J., 2nd (see *Huggins, M. L.*)
 Fieldner, A. C., Katz, S. H., and Kinney, S. F. 386
 Fieldner, A. C., Oberfell, G. G., Teague, M. C., and Lawrence, J. N. 25
 Figuier, L. 1
 Figuier, P. 1
 Filhol, E. 3
 Finazzi, F. (see *Bellati, M.*)
 Finch, G. I., and Stimson, J. C. 267
 Fink, C. G. 305; (see *Bodenstein, M.*)
 Finzel, T. G. 319
- Firth, J. B. 8, 9, 47, 65, 83, 86, 88, 90, 93, 119, 213, 290, 297, 298; (see *Driver, J.*; *Fells, H. A.*; *Holt, A.*)
 Firth, J. B., and Watson, F. S. 94
 Fischer, F. 292, 397, 399
 Fisher, E. A. 186, 380
 Fizeau, H. 54
 Fleischer, A. 126, 438
 Fleming, H. 380
 Flodorf, E. W. (see *Kistiakowsky, G. B.*)
 Flodorf, E. W., and Kistiakowsky, G. B. 208, 404, 411, 423
 Flusin and Barry 385
 Fontana, F. 1, 17
 Foote, H. W., and Dixon, J. K. 210
 Foote, H. W., and Saxton, B. 186
 Footitt, F. F. (see *Washburn, E. W.*)
 Foresti, B. 316, 421
 Francis, M., and Burt, F. P. 48, 51, 241
 Francis, W., and Wheeler, R. V. 122
 Frank, H. S. 229
 Frankenburger, W. 499; (see *Fajans, K.*)
 Frankenheim, M. L. 7
 Frazer, J. C. W. 499, 500
 Frazer, J. C. W., Patrick, W. A., and Smith, H. E. 225, 230, 231, 234, 236, 305
 Frazer, J. H. 231, 232, 253, 254, 329; (see *Herzfeld, K.*)
 Fremery, W. (see *Willstätter, R.*)
 Frenkel, J. 149, 482, 486, 495
 Frenzel, W. 386
 Fresenius, H. 317
 Freudenberg, K. 360
 Freundlich, H. 5, 32, 41, 65, 96, 107, 116, 126, 164, 424, 485, 493
 Freundlich, H., and Bjercke, A. 121
 Freundlich, H., and Losev, G. 5

- Freundlich, H., and Sachs, W. 393
 Friedel, G. 167, 171, 395
 Fritzman, E. 259
 Frolich, K., and White, A. 113
 Frumkin, A. 495
 Frydlender, J. H. 393
 Fryling, C. F. 310, 417
 Fu, Y. (see *Bartell, F. E.*)
 Fürth, R. (see *Gicklhorn, J.*)
 Fuwa, T. 371 (see *Venable, C. S.*; *Wilson, R. E.*)
 Fuwa, T., and Godbout, A. P. 378

 Gaede, W. 233
 Gahn, P. J. 1
 Galitzine, Prince B. 458
 Ganguli, A. 412, 484; (see *Kar, K. C.*)
 Gans, D. M. (see *Harkins, W. D.*)
 Garner, W. E. 347, 419, 494, (see *Blench, E. A.*; *Bull, H. I.*)
 Garner, W. E., and Kingman, F. E. T. 10, 72, 347
 Garner, W. E., and McKie, D. 404, 417, 419, 420
 Garner, W. E., McKie, D., and Knight, B. C. J. G. 347
 Garrett, E. A. 380
 Gates, S. F. (see *Lambert, R.*)
 Gaudechon, H. 147, 410
 Gauger, A. W. 306, 311, 315, 396; (see *Larian, M.*; *Lavine, I.*)
 Gauger, A. W., and Taylor, H. S. 309, 312, 316
 Gaunt, H., and Usher, F. L. 186
 Gebhardt, H. (see *Gutbier, A.*)
 Gehler, J. S. T. 7
 Gehlhoff, G., and Schmidt, R. 337
 General Electric Co., Research Staff of 216
 George, H. J. (see *Evans, M. H.*)
 George, H. T. (see *Willows, R. S.*)
 Georgievics 8
 Germer, L. H. 322, 487; (see *Davisson, C. J.*)
 Gerum, J. (see *Paal, C.*)
 Gibbons and Smith 386
 Gicklhorn, J., Fürth, R., and Blüh, O. 516
 Giebenhain, H. (see *Magnus, A.*)
 Giesen, J. 23, 119, 222
 Giffen, F. J. (see *Kenrick, F. B.*)
 Gilbert, H. N. 481
 Gillespie, D. C. (see *Burk, R. E.*)
 Gillespie, L. J., and Hall, F. P. 298, 299, 300, 421
 Glatzel, G. (see *Simon, F.*)
 Godbout, A. P. (see *Fuwa, T.*)
 Goergen, S. M. (see *Pearce, J. N.*)
 Goertz, M. (see *Obermiller, J.*)
 Goldmann, F., and Polányi, M. 18, 22, 86, 87, 88, 125, 126, 127, 135, 138, 139, 141, 143, 412, 413, 414, 415, 459
 Gomolka, F. (see *Stock, A.*)
 Good, S. J. 372
 Goodwin, N., and Park, C. R. 67, 88
 Gorbatschew, A. 485, 486
 Gotta, A. (see *Sieverts, A.*)
 Goucher, F. S., and Ward, H. 349
 Gouy, M. 217
 Graf, F. 283
 Graham, G. B. (see *Stewacie, E. W. R.*)
 Graham, J. I. 107, 108; (see *Coles, G.*)
 Graham, T. 1, 9, 260, 265, 281, 288, 289, 292, 300, 384, 386, 397, 399
 Graham, T., and Hofmann, A. W. 4
 Grähling, K. (see *Magnus, A.*)
 Grandjean, F. 167, 169, 175
 Granovskii, V. I. 245
 Gray, H. LeB., and Staud, C. J. 358
 Gregg, S. J. 93, 105, 401, 408, 435, 491, 527
 Greider, C. E. (see *Patrick, W. A.*)
 Griffin, C. W. 317
 Griffith, A. A. 22, 226, 330, 507
 Griffith, I. 529

- Griffiths, E. 371
 Grimm, F. V. (see *Patrick, W. A.*)
 van der Grinten, K. 336
 Grosheintz, K. 385
 Gross, R., and Volmer, M. 465
 Grunmach, L. 386
 Grzenkowski, M. (see *Henglein, F. A.*)
 Guichard, M. 24, 193, 201, 216, 316
 Guntz, A. (see *Berthelot, M.*)
 Gurwitsch, L. 147
 Gurwitsch, L. G. 135, 139, 203, 395, 410, 437
 Gustafson, B. 134, 152
 Gustaver, B. 47, 52, 134, 140, 152, 194, 330
 Gutbier, A. 284
 Gutbier, A., Gebhardt, H., and Ottenstein, B. 283, 289, 290
 Gutbier, A., and Maisch, O. 281
 Gutbier, A., Ottenstein, B., and Weise, G. L. 283
 Gutbier, A., and Schieferdecker, W. 283, 296

 Haak, J. J. 270, 271, 272
 Haak, J. J., and Sissingh, R. 253, 270
 Haber, F. 464
 Hackl, O. 386
 Haenni, P. (see *Kohlschütter, V.*)
 Hagen, H. 266
 Hagen, H., and Sieverts, A. 260
 Hagenacker, J. (see *Sieverts, A.*)
 von Hahn, F. V. 339
 Hahn, O. 203
 Hahn, O., and Biltz, M. 203
 Hahn, O., and Imre, L. 333
 Hall, A. J. 362
 Hall, F. P. (see *Gillespie, L. J.*)
 Hall, W. J. (see *Shorter, S. A.*)
 Halla, F. 292
 Haller, W. (see *Ostwald, W.*)
 Hällström, M. af 140, 154, 194
 Hamburger, L. 44

 Hammerschmidt, W. (see *Thiel, A.*)
 Hampe, W. 317
 Hanawalt, J. D. 301
 Hand, P. G. T. (see *Allmand, A. J.*)
 Hand, P. G. T., and Shiels, D. O. 67, 77, 86, 144, 150
 Hannay, J. B. 214
 Harding, E. A., and Smith, D. P. 292, 396, 398
 Hardy, W. B. 348, 350, 351, 466, 510, 511
 Hardy, W. B., and Nottage, M. 350, 428, 497
 Harkins, W. D., and Ewing, D. T. 87, 88, 147, 447
 Harkins, W. D., and Gans, D. M. 275
 Harmon, F. C. 59
 Harned, H. S. 23, 51, 52, 93
 Harris, J. E., and Schumacher, E. E. 215, 210, 222, 240
 Harrison, E. W. (see *Laing, M. E.*)
 Harrison, H. K. 372
 Harteck, P. (see *Bonhoeffer, K. F.*)
 Hartley, H. 266
 Hartmann, C. A., and Dossmann, H. 66
 Hartshorne, W. D. 371, 378, 379, 380
 Harvey, C. E. (see *McBain, J. W.*)
 Hauser, E. A. 360, 384; (see *Bary, P.*)
 Hautefeuille, P. (see *Troost, L.*)
 Hayashi, K. 85; (see *Sameshima, J.*)
 Heald, W. 307
 Hedelius, A. H. (see *von Euler, H.*)
 Hedges, J. J. 371, 379, 425; (see *Barker, S. G.*)
 Hedvall, J. A. 390
 Heim, C. 93
 Hempel 386
 Hempel, W., and Thiele, H. 308

- Hempel, W., and Vater, G. 65,
102, 162
de Hemptinne, A. 96, 279, 290,
313
Hendricks, B. C. (see *Deming*,
H. G.)
Hendricks, B. C., and Ralston,
R. R. 263
Hendricks, S. B. 81, 82
Hene, W. 77, 100, 163
Henglein, F. A., and Grzenkowski,
M. 24, 119
Henri, V. 386
Henry, D. C. 32, 430, 489, 490,
493
Herbert, J. B. M. 48, 256
Herbst, H. 51, 59, 61, 67, 72, 81,
84, 119, 154
Herlinger, E. (see *Eitel*, W.)
Hertlein, H. F. 525
Hertz, H. 465
Herzberg, G. (see *Kautsky*, H.)
Herzfeld, K., and Frazer, J. H.
231
Herzfeld, K. F. 418, 422, 525
Herzog, A. 371
Herzog, R. O. 371
Hess, K., and Trogus, C. 360
Hess, K., Trogus, C., Ljubitsch,
N., and Akim, L. 360
Hey, M. H. 168
Heyn 387
Heyn, E. 396
Heynemann, H. (see *Stock*, A.)
Hildebrand, J. H. 438
Hilditch, T. P. 499; (see *Arm-*
strong, E. F.)
Hill, A. V. 472
Hill, J. A. 380
Hill, S. E. 217, 387
Hinshelwood, C. N. 499; (see
Donnelly, R. P.)
Hinteler, B. (see *Schmidt*, G. C.)
Hirata, M. 67, 439
Hirsch, A. (see *Kautsky*, H.)
Hirst, H. R. (see *Shorter*, S. A.)
Hirst, M. C. (see *Speakman*, J. B.)
Hitchcock, D. I. 473
Hock, L. 383
Hock, L., and Barth, W. 383
Hockin, L. E. (see *Travers*, M.
W.)
Hoffert, W. H. 178
Hofmann, A. W. (see *Graham*, T.)
Hofmann, K. A., and Hofmann,
U. 66
Hofmann, K. A., and Röchling, C.
66
Hofmann, U. 66, 67; (see *Hof-*
mann, K. A.)
Hohlfeld, E. (see *Ruff*, O.)
Hoitsema, C. 289, 296, 297
Holmes, H. N., and Anderson,
J. A. 181
Holmes, H. N., Sullivan, R. W.,
and Metcalf, N. W. 181
Holmes, H. N., and Weide, H. F.
200
Holt, A. 298; (see *Andrew*,
J. H.)
Holt, A., Edgar, E. C., and Firth,
J. B. 8, 289, 298
Homfray, I. F. 11, 18, 31, 43, 55,
86, 97, 98, 99, 100, 101, 114, 116,
118, 156, 157, 158, 162, 429, 452,
454, 455, 456, 473, 477, 478, 484,
491, 492
Hönig 382
Honig, P. 76, 77
Hoover, G. I., and Rideal, E. K.
205, 411
Hoskins, W. M., and Bray, W. C.
500
Houghton, A. S. 385
Howard, H. C., and Hulett, G. A.
46, 67, 68, 90, 91, 92, 102.
d'Huart, 224
Huber, H., Kirschfeld, L., and
Sieverts, A. 261, 293
Hückel, E. 483, 486, 494, 495, 512,
525
Hufner, G. 385

- Huggins, M. L., and Field, J., 2nd 481
 Hulett, G. A. 410; (see *Burns, R. M.*; *Cude, H. E.*; *Howard, H. C.*; *Lowry, H. H.*; *Nelson, O. A.*)
 Hull, A. W. 302
 Hunter, J. 2, 104, 107, 119, 135
 Hurst, W. W., and Rideal, E. K. 318, 495
 Husson, A. (see *Vavon, G.*)
 Hutchinson, C. W. 372
 Hüttig, G. F. 168; (see *Biltz, W.*)
 Hüttig, G. F., and Juza, R. 158
 Ihmori, T. 23, 222, 246, 247, 276, 329; (see *Warburg, E.*)
 Iliin, B. 51, 346, 483, 485, 526, 527
 Iliin, B., and Rosanow, B. 424
 Imre, L. (see *Hahn, O.*)
 Ingersoll, L. R. 398
 Iredale, T. 275, 330
 Ising, G., and Urelius, N. 246
 Isobe, H. 144, 160, 197
 Isselstein, M. T. 237, 338
 de Izaguirre, R. (see *Ostwald, Wo.*)
 Jaag, E. (see *Bosshard, E.*)
 Jackman, D. N. (see *McBain, J. W.*; *Parker, R. G.*)
 Jaeckel, G. 258
 Jamin, J., and Bertrand, A. 220
 Jaquet, E. 32, 55, 347, 483, 484, 489, 520, 523
 Jarman, J. (see *Philip, J. C.*)
 Jenkins, W. J., and Bennett, H. B. 24, 372, 375
 Joffé, A. F. 329
 Johnsen, A. 168
 Johnson, C. R. 70, 78
 Johnson, F. M. G. (see *Munro, L. A.*; *Steacie, E. W. R.*)
 Johnson, F. M. G., and Larose, P. 262, 264, 266
 Johnson, M. C. 245, 421, 465
 Johnston, J. (see *Andrews, D. H.*)
 Johnston, J., and Leopold, H. G. 385
 Johnstone, H. F. (see *Pearce, J. N.*)
 Jones, D. C. 249, 329; (see *Patrick, W. A.*)
 Jones, D. C., and Outridge, L. 200
 Josse 387
 Joulin, L. 7, 103, 114, 115, 160
 Jungk, C. G. 423
 Jurisch, E. 266; (see *Sieverts, A.*)
 Juza, R. (see *Hüttig, G. F.*)
 Kälberer, H., Mark, H., and Schuster, C. 40, 484
 Kälberer, W. (see *Magnus, A.*)
 Kälberer, W., and Mark, H. 194, 195, 196, 321, 331, 405
 Kälberer, W., and Schuster, C. 40, 195, 405
 Kamienski, B. 321
 Kanata, K. 384, 387
 Kaplan, B. B. (see *Selvig, W. A.*)
 Kar, K. C., and Ganguli, A. 484, 493, 527
 Kar, S. C. 484
 Kasai, K. 337, 339, 340
 Katz, J. R. 147, 150, 167, 193, 248, 249, 250, 358, 376, 377, 383, 385, 442, 451
 Katz, J. R., and Bing, K. 383
 Katz, S. H. (see *Fieldner, A. C.*)
 Kaul, L. 261, 263
 Kausch, O. 58, 78
 Kautsky, H. 170, 175
 Kautsky, H., and Blinoff, G. 170, 175
 Kautsky, H., and Herzberg, G. 175
 Kautsky, H., and Hirsch, A. 175
 Kautsky, H., and Neitzke, O. 175
 Kautsky, H., and Thiele, H. 175
 Kautsky, H., and Zocher, H. 175
 Kayser, H. 7, 17, 114, 115, 240, 385, 464, 495
 Keesom, W. H. 516

- Kenrick, F. B., and Giffen, F. J.
219, 393
- Keyes, F. G. 512
- Keyes, F. G., and Felsing, W. A.
28
- Keyes, F. G., and Marshall, M. J.
123, 147, 347, 416, 419, 496,
526
- Kieffer, R. (see *Magnus, A.*)
- Kimura, R. 378, 379
- King, A. T. 380 (see *Barritt, J.*)
- King, J. E. (see *Bakr, A. M.*)
- King, R. B. (see *Allmand, A. J.*)
- Kingdon, K. H. 268; (see *Lang-
muir, I.*)
- Kingdon, K. H., and Langmuir, I.
268
- Kingman, F. E. T. 43; (see *Garner,
W. E.*)
- Kinney, S. F. (see *Fieldner, A. C.*)
- Kirchner, F. 278
- Kirchhof, F. 385
- Kirschfeld, L. (see *Huber, H.*)
- Kirschfeld, L., and Sieverts, A.
261
- Kistiakowsky, G. B. 422, 423;
(see *Flosdorf, E. W.*; *Taylor,
G. B.*; *Taylor, H. S.*)
- Kistiakowsky, G. B., Flosdorf,
E. W., and Taylor, H. S. 417
- Kistler, S. S. 180
- Klein, W. 167
- Klit, A. (see *Bülmann, E.*)
- Klosky, S. 204
- Klosky, S., and Burggraff, A. J.
204
- Klosky, S., and Marzano, C. 204
- Klosky, S., and Woo, L. P. L. 204
- Knecht, E., Rawson, C., and
Loewenthal, R. 381
- Knight, B. C. J. G. (see *Garner,
W. E.*)
- Knott, C. G. 399
- Knudsen, M. 465, 482
- Knudson, C. M. 55, 119, 140, 154;
(see *Pearce, J. N.*)
- Kobayashi, Y. 495; (see *Kujirai,
T.*)
- Kobbe 387
- Kobe, K. (see *Reyerson, L. H.*)
- Kobe, K. A. 69
- Koch-Holm, E. 67
- Kohlschütter, V., and Haenni, P.
176
- Kohman, G. T. 385; (see *Lowry,
H. H.*)
- König, M. 272
- Kotowski, A. (see *Pietsch, E.*)
- Kowalewsky, S. N. 381
- Kracek, F. C. 22
- Krauschkina, L. (see *Rehbinder,
P.*)
- Krakau, A. 399
- Kratky, O. (see *Eckling, K.*)
- Kratz, H. (see *Magnus, A.*)
- Kraus, C. A., and Darby, E. H.
214
- Krause, H. 238
- Kraut, H. (see *Willstätter, R.*)
- Krczil, F. 61, 62, 71, 76, 79,
425
- Kremann, R. 349
- Krestinskii, V. N. 120
- Kroeker, K. 5, 485
- Krüger, F., and Sacklowski, A.
288, 302, 398
- Krüll, F. (see *Sieverts, A.*)
- Krumbhaar, W. (see *Sieverts, A.*)
- Kruyt, H. R. 502
- Kruyt, H. R., and van Duin, C. F.
502
- Kruyt, H. R., and Modderman,
J. G. 400, 423, 424
- Kruyt, H. R., and van der Spek,
Jac. 424
- Kubota, B., and Yoshikawa, K.
315
- Kujirai, T., Kobayashi, Y., and
Toriyama, Y. 378
- Kundt, A., and Warburg, E. 223
- Küster, F. W. 4
- Kutzelnigg, A. 121

- Lachman, F. (see *Lachs, H.*)
 Lachs, H., and Lachman, F. 424
 Lagergren, S. 51, 423, 447
 Laing, M. E., McBain, J. W., and Harrison, E. W. 275
 Lamb, A. B. 169
 Lamb, A. B., and Coolidge, A. S. 137, 401, 402, 407, 408, 409, 410, 447, 452
 Lamb, A. B., Wilson, R. E., and Chaney, N. K. 25, 47, 60, 65, 66, 69, 72, 73, 495
 Lambert, B., and Clark, A. M. 185, 187, 188, 189, 190, 191
 Lambert, R., and Gates, S. F. 298
 Lambourn, L. J. (see *Shakespear, G. A.*)
 Landé, A. (see *Lorenz, R.*)
 Landolt, H. 213
 Landt, E., and Volmer, M. 354, 355
 Langmuir, I. 5, 8, 10, 15, 32, 40, 41, 69, 123, 137, 138, 149, 218, 219, 224, 235, 251, 252, 261, 266, 269, 271, 277, 278, 285, 317, 325, 326, 329, 331, 353, 356, 372, 373, 378, 410, 428, 430, 437, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 489, 490, 493, 494, 495, 497, 498, 499, 500, 501, 504, 506, 527; (see *Kingdon, K. H.*)
 Langmuir, I., and Kingdon, K. H. 268, 356, 401, 494, 520
 Langmuir, I., and Sweetser, S. P. 243, 251
 Langmuir, I., and Villars, D. S. 268, 269, 401, 520
 Lanning, C. E. 210
 Lannung, A. 41
 Lapkamp, K. (see *Seeliger, R.*)
 Larian, M., Lavine, I., Mann, C. A., and Gauger, A. W. 154
 Larose, P. (see *Johnson, F. M. G.*)
 Latham, G. H. 234, 305, 306
 Latimer, W. M.
 Latreille, H. (see *Mcunier, L.*)
 Lavine, I. (see *Larian, M.*)
 Lavine, I., and Gauger, A. W. 154, 406
 Lawrence, A. S. C. 352
 Lawrence, J. N. (see *Fieldner, A. C.*)
 Lazier, W. A. (see *Adkins, H.*)
 Lazier, W. A., and Adkins, H. 206
 Le Chatelier, H. 213
 Lemon, H. B. 52, 59, 65, 68, 70
 Lemon, H. B., and Blodgett, K. 103, 160, 162
 Lenher, S. 193, 224, 227, 235, 305; (see *McHaffie, I. R.*)
 Lenher, S., and McHaffie, I. R. 193, 224, 226, 305
 Lenher, V. 68
 Lennard-Jones, J. E., and Dent, B. M. 252, 327, 329, 516, 517, 518, 519
 Leopold, H. G. (see *Johnston, J.*)
 Lepin, L. K. (see *Shilov, N. A.*)
 Leprince-Ringuet, F. 107
 Lester, J. H. 365, 371
 Leslie, E. H., and Carr, A. R. 22
 Lewin, G. (see *Weber, L. I.*)
 Lewis, W. C. McC. 275
 Liesegang, R. E. 61
 Linde, J. O., and Borclius, G. 301, 302, 399
 Lisenko 289
 Ljubitsch, N. (see *Hess, K.*)
 Lobinger, K. (see *Willstätter, R.*)
 Loeb, L. B. 282, 465
 Loewenthal, R. (see *Knecht, E.*)
 Lohrmann, V. 378
 Lombard, V. 263
 Lo Monaco, D. 14
 London 471
 Long, J. S. (see *Patrick, W. A.*)
 Longinescu, G. G., and Theodosiu, C. N. 119
 Loomis, A. G., and Smith, D. F. 242

- Lorenz, L. 26
 Lorenz, R. 22
 Lorenz, R., and Landé, A. 56, 516, 520, 522, 523
 Lorenz, R., and Wiedbrauck, E. 25, 52, 161, 166
 Losev, G. (see *Freundlich, H.*)
 Love, K. S. (see *Emmett, P. H.*)
 Lowitz, T. 1
 Lowry, H. H. 24, 59, 67, 70, 71, 88, 153, 344; (see *Murphy, E. J.*)
 Lowry, H. H., and Bozorth, R. M. 67, 71
 Lowry, H. H., and Hulett, G. A. 3, 9, 58, 69, 86, 105, 106, 123, 146, 153, 344, 441
 Lowry, H. H., and Kohman, G. T. 384, 385
 Lowry, H. H., and Morgan, S. O. 67, 71, 123
 Lowry, H. H., and Olmstead, P. S. 448, 451, 455, 456, 457
 Lucas, H. P. (see *McBain, J. W.*)
 Luce, L. R. 307, 485
 Luft, F. (see *Eggert, J.*)
 Lux, H. 120

 Maass, O. (see *Pidgeon, L. M.*)
 McAulay, A. L., and Mellor, D. P. 340
 McBain, J. W. 5, 6, 8, 11, 41, 44, 45, 46, 47, 59, 61, 80, 92, 93, 94, 125, 128, 129, 132, 139, 140, 141, 142, 146, 148, 169, 180, 186, 233, 266, 269, 271, 272, 273, 330, 331, 348, 350, 351, 354, 359, 372, 374, 391, 394, 400, 424, 430, 438, 440, 444, 473, 481, 486, 488, 489, 524, 525; (see *Alexander, J.*; *Bakr, A. M.*; *Laing, M. E.*)
 McBain, J. W., and Bakr, A. M. 19, 20, 23
 McBain, J. W., and Britton, G. T. 14, 44, 64, 109, 110, 347, 459, 460, 473, 497
 McBain, J. W., and Davies, G. P. 275, 348, 444
 McBain, J. W., and DuBois, R. 275, 348, 444
 McBain, J. W., and Ferguson, J. 211, 390, 406
 McBain, J. W., Jackman, D. N., Bakr, A. M., and Smith, H. G. 61, 128, 129, 130, 438
 McBain, J. W., Lucas, H. P., and Chapman, P. F. 128, 129, 130, 140, 148, 306, 434, 438
 McBain, J. W., Smith, L. E., and Harvey, C. E. 375
 McBain, J. W., and Tanner, H. G. 19, 496
 McElfresh, W. E. 399
 McGavack, J., Jr., and Patrick, W. A. 179, 184, 194, 195, 434, 435, 437, 438, 441
 McHaffie, I. R. (see *Lenher, S.*)
 McHaffie, I. R., and Lenher, S. 146, 224, 225, 227, 228, 230, 234, 305
 McKeehan, L. W. 259, 302, 398
 McKie, D. 347, 404, 419; (see *Garner, W. E.*)
 McKinley, L. 401; (see *Pearce, J. N.*)
 McKinley, L., and Pearce, J. N. 401
 McLaughlin, R. R. (see *Boswell, M. C.*)
 McLean, S. 10, 43, 90, 121, 122, 156, 417
 Macy, R. 63
 Magli, G. (see *Piutti, A.*)
 Magnus, A. 56, 81, 94, 405, 417, 485, 495, 514, 521, 525
 Magnus, A., and Braner, M. 405, 521
 Magnus, A., and Cahn, L. 117
 Magnus, A., and Giebenhain, H. 198, 405

- Magnus, A., and Grähling, K. 195,
 405
 Magnus, A., and Kälberer, W. 194,
 404, 417
 Magnus, A., and Kieffer, R. 40,
 198, 199, 405
 Magnus, A., and Kratz, H. 59, 117,
 405
 Magnus, A., and Müller, A. 199
 Magnus, A., and Roth, H. 165, 521,
 524
 Magnus, A., Sauter, E., and Kratz,
 H. 117, 405
 Magnus, G. 114, 240
 Mahnert, P. (see *Volmer, M.*)
 Maier, L. (see *Bachmann, W.*)
 Maisch, O. (see *Gutbier, A.*)
 Malaguti and Durocher 167
 Mallard, E. 167
 Manley, J. J. 217, 219
 Mann, C. A. (see *Larian, M.*)
 Manning, J. E. (see *Allmand, A.*
J.)
 Manville, O. 122
 Marc, R. 334
 Marcelin, R. 251, 465
 Marcet, F. 53, 220
 Mark, H. (see *Dunkel, M.*; *Käl-*
berer, H.; *Kälberer, W.*; *Meyer,*
K. H.)
 Markham, E. C., and Benton,
 A. F. 200
 Marshall, M. J. (see *Keyes, F. G.*;
Wright, R. H.)
 Marshall, M. J., and Bramston-
 Cook, H. E. 347, 402, 403, 418
 Martin, A. E. 465
 Martin, G. 337
 Martini, T. 193, 424
 Marxen, J. (see *Drucker, C.*)
 Marzano, C. (see *Klosky, S.*)
 Maschke 181
 Masson, I. 43, 169, 520
 Masson, I., and Dolley, L. G. F.
 520
 Masson, O. 223, 364
 Masson, O., and Richards, E. S.
 364, 371
 Masucci, P., and Moffat, M. I. 387
 Matalski, V. (see *Alexejew, D.*)
 Matthew, J. A. (see *Preston, M. H.*)
 Mauersberger, H. R. 371, 381
 Mautner, P. 400
 Maxted, E. B. 280, 303, 304, 423,
 503
 Mayer, E. C. 213
 Mayer, M., and Altmayer, V. 308
 Mecklenburg, W. 61
 Meehan, F. T. 211, 390
 Mehlhorn, F., (and Warburg, E.)
 239
 Mellor, D. P. (see *McAulay, A. L.*)
 Melsens 120, 317, 406
 Mendenhall, C. E. 323
 Menon, A. S. (see *Watson, H. E.*)
 Menzies, A. W. C. 212, 216, 223
 Metcalf, N. W. (see *Holmes, H. N.*)
 Metz, A. (see *Sieverts, A.*)
 Meunier, L., and Latreille, H. 381
 Meyer, J. 349
 Meyer, K. H., and Mark, H. 360
 Meyerhof, O., and Weber, H. 121
 Milbourn, M. (see *Miles, F. D.*)
 Miles, F. D., and Craik, J. 360, 371
 Miles, F. D., and Milbourn, M. 371
 Miller, E. B. 178
 Milligan, L. H. 203
 Mills, E. J., and Takamine, J. 51
 Mills, E. J., and Thomson, G. 51
 Miravalles, R. (see *Moles, E.*)
 Mitchell 386
 Mitscherlich, M. E. 3, 214, 278,
 447, 449, 452
 Mittasch, A. 508
 Mitton, R. G. 270
 Modderman, J. G. (see *Kruijt, H.*
R.)
 Moffat, M. I. (see *Masucci, P.*)
 Mohr, W. 159
 Moles, E. (see *Crespi, M.*)
 Moles, E., and Crespi, M. 242
 Moles, E., and Miravalles, R. 242

- Moll, F. 355
 Mond, L., Ramsay, W., and Shields, J. 265, 278, 279, 281, 289, 291, 296, 421, 424
 Monro, A. D. 85
 Montonna, R. E. 358
 Morávek, V. 481
 Morey, G. W. 220
 Morgan, S. O. 457; (see *Lowry, H. H.*)
 Morozzo, C. L. 2
 Morris, V. N., and Street, J. N. 387
 de Morveau, L. B. G. 2
 Moser, L. 54, 220
 Moses, W. (see *Sabalitschka, T.*)
 Mugden, S. (see *Ruff, O.*)
 Mülfarth, P. 236, 239
 Müller, A. (see *Magnus, A.*)
 Müller, E. 379
 Müller, E., and Schwabe, K. 279, 282, 284, 285, 289, 293
 Müller-Goldegg, G. (see *Sieverts, A.*)
 Müller-Erzbach, W. 203, 447, 450
 Munro, L. A., and Johnson, F. M. G. 203, 442
 Murphy, D. W. (see *Carr, A. R.*)
 Murphy, E. J., and Lowry, H. H. 356
 Murphy, E. J. (see *Williams, R. R.*)

 Nara, M. (see *Oguri, S.*)
 von Náray-Szabó, St. 376
 Neal, A. M. (see *Williams, I.*)
 Neale, S. M. 371
 Negelein, E. (see *Warburg, O.*)
 Neitzke, O. (see *Kautsky, H.*)
 Nellensteyn, F. J. 15
 Nelson, O. A., and Hulett, G. A. 371
 Netzke, 68
 Neumann, B. 266, 320
 Neumann, G., and Streintz, F. 282, 308
 Neville, H. A. (see *Taylor, H. S.*)
 Newbery, E. 292, 398

 Newsome, P. T. 19; (see *Shepard, S. E.*)
 Nicol, J. (see *Richardson, O. W.*)
 Nikitin, N. 198, 200, 310, 311, 312, 313, 316, 319, 320
 Nikitin, N. I., and Sharkov, V. I. 310, 319
 Nikitin, N. I., and Yuryev, V. I. 205
 Nishizawa, K. (see *Traube, J.*)
 Nissen, B. H. (see *Adkins, H.*)
 Norzi, G. (see *Porlezza, C.*)
 Nottage, M. (see *Hardy, W. B.*)
 Nutting, P. G. 246, 344, 451

 Oberfell, G. G. (see *Fieldner, A. C.*)
 Obermiller, J. 371, 381
 Obermiller, J., and Goertz, M. 381, 382
 O'Connor, E. A. (see *Bowden, F. P.*)
 Oddo, B. 377
 Oden 330
 Ogawa, I. 67, 77
 Oguri, S., and Nara, M. 364
 Ohya, T. (see *Davey, W. C.*)
 Okatov, A. P. 120, 200, 405; (see *Sapozhnikov, A. V.*)
 Okazawa, T. 65, 147, 415
 Olbrich, W. (see *Ruff, O.*)
 Oliphant, M. L. 273, 274
 Oliphant, M. L., and Burdon, R. S. 273, 330
 Olmstead, P. S. (see *Lowry, H. H.*)
 Opdycke, L. H. (see *Patrick, W. A.*)
 d'Or, L. 242
 Osawa, A. 278, 302, 397, 398
 Osterhof, H. J. (see *Bartell, F. E.*)
 Ostwald, Wilhelm I, 114, 238, 432, 498
 Ostwald, Wo. 472, 499
 Ostwald, Wo., and Haller, W. 393
 Ostwald, Wo., and de Izaguirre, R. 5
 Ott, E. 376
 Ottenstein, B. (see *Gutbier, A.*)
 Outridge, L. (see *Jones, D. C.*)

- Owens, A. E. (see *Patrick, W. A.*)
 Oxley, A. E. 300, 301
- Paal, C., and Amberger, C. 289
 Paal, C., and Auerswald, C. 282
 Paal, C., and Gerum, J. 289, 292
 Page, A. B. P. 75, 76
 Pal, M. N. (see *Chowdhury, J. K.*)
 Palkin, A. P. 168
 Palmer, W. G. 25, 276, 421, 481, 523, 525
 Paneth, F. 42, 333, 336, 337, 340
 Paneth, F., and Peters, K. 214, 283
 Paneth, F., and Radu, A. 334, 335, 336, 339
 Paneth, F., and Thimann, W. 334, 335, 353
 Paneth, F., and Vorwerk, W. 333, 334
 Paramasivan, S. 67
 Paranjpe, G. R. 193, 235
 Park, C. R. (see *Goodwin, N.*)
 Parker, R. G., and Jackman, D. N. 381
 Parks, G. J. 193, 223, 344, 423, 425
 Parnell, E. A. 381
 Parnell, T. (see *Richardson, O. W.*)
 Pascal, P. 186
 Patrick, W. A. 119, 184, 194, 424, 432, 433, 434, 435, 452; (see *Davidheiser, L. Y.*; *Frazer, J. C. W.*; *McGavack, J., Jr.*)
 Patrick, W. A., Davis, P. B., and Barclay, E. H. 184
 Patrick, W. A., and Eberman, N. F. 444
 Patrick, W. A., and Greider, C. E. 180, 194, 413, 435
 Patrick, W. A., and Grimm, F. V. 424
 Patrick, W. A., and Jones, D. C. 440
 Patrick, W. A., and Long, J. S. 194, 197, 198
 Patrick, W. A., and Opdycke, L. H. 185, 200
- Patrick, W. A., Preston, W. C., and Owens, A. E. 196, 197, 444
 Patterson, T. L. 78
 Pauling, L. 168, 511
 Pavlov, P. N. 392
 Payen 387
 Pearce, J. N. (see *McKinley, L.*)
 Pearce, J. N., and Alvarado, A. M. 203, 205
 Pearce, J. N., and Goergen, S. M. 205
 Pearce, J. N., and Johnstone, H. F. 125, 131, 401, 463
 Pearce, J. N., and Knudson, C. M. 110, 140, 154
 Pearce, J. N., and McKinley, L. 401, 407
 Pearce, J. N., and Reed, G. H. 407
 Pearce, J. N., and Rice, M. J. 205
 Pearce, J. N., and Taylor, A. L. 125, 401
 Pearce, T. J. P. (see *Travers, M. W.*)
 Pease, R. N. 317, 318, 503
 Pease, R. N., and Stewart, L. 308, 317, 503, 504
 Peirce, F. T. 364
 Perrin, J. 348
 Perry, J. H. 203; (see *Taylor, G. B.*)
 Peters, K. (see *Paneth, F.*)
 Peters, K., and Weil, K. 156, 157, 193
 Pettijohn, E. 232
 Peyron, 387
 Pfeiffer, E. W. R. 107
 Philip, J. C. 191
 Philip, J. C., Dunnill, S., and Workman, O. 75
 Philip, J. C., and Jarman, J. 65
 Pickard, R. H. 359, 365, 370
 Pickering, S. F. (see *Edwards, J. D.*)
 Pickles, A. 47, 86
 Pickles, S. S. 67
 Pidgeon, L. M., and Maass, O. 370

- Pietsch, E. 218; (see *Schwab, G. M.*)
 Pietsch, E., Kotowski, A., and Berend, G. 507
 Pirani, M. 217
 Piutti, A. 78
 Piutti, A., and Magli, G. 84
 Planck 484
 Plummer, W. B. 151
 Podrouzek, V. 509
 Poggendorff, J. C. 397
 Pohl, R. 217
 Polányi, M. 83, 428, 430, 447, 450, 452, 457, 458, 459, 461, 463, 471, 473, 477, 478, 484, 487, 488, 489, 500; (see *Eyring, H.*; *Goldmann, F.*)
 Polányi, M., and Welke, K. 39, 117, 416, 418, 459
 Polányi, Mihály 245
 Pollard, F. H. 280, 282
 Polyakov, M. V. 267
 Pool, B. (see *Trouton, F. T.*)
 Porlezza, C., and Norzi, G. 159
 Porritt, B. D., and Allen, W. S. 387
 Porter, A. W. 500
 Porter, J. L. 88, 148, 154, 344, 391, 394, 430
 Pouillet, C. M. 423
 Preston, F. W. 213
 Preston, M. H., and Matthew, J. A. 371
 Preston, W. C. (see *Patrick, W. A.*)
 Priestley, J. 2
 Priestley, L. P. (see *Barker, J.*)
 Priestman, H. 381
 Purcell, R. (see *Smits, A.*)
 von Putnok, L., and von Szelényi, G. 200
 Puttick, A. (see *Allmand, A. J.*)
 Quincke, G. 53, 250, 251, 271, 349
 Radu, A. (see *Paneth, F.*)
 Rahlfs, E. (see *Bilz, W.*)
 Rakovsky, A. V. 147, 150, 376, 378
 Rakusin, M. A. (see *Zelinsky, N. D.*)
 Ralston, R. R. (see *Hendricks, B. C.*)
 Ramsay, W. 157, 266, 298; (see *Mond, L.*)
 Rankine, A. O. 81
 Rankine, A. O., and Smith, C. J. 81
 Rawson, C. (see *Knecht, E.*)
 Ray, A. B. 66, 74; (see *Chaney, N. K.*)
 Ray, R. C. 200
 Rayleigh 387
 Rayleigh, Lord 451
 Raynes, J. L. 381
 Rebbeck, J. W., and Ferguson, J. B. 216, 217, 218, 224
 Reboul, G. 307
 Rector, T. M. 386
 Reed, G. H. (see *Pearce, J. N.*)
 Reeser, C. A. 270, 271, 272
 Reeser, C. A., and Sissingh, R. 26, 270
 Rehbinder, P., and Krajuschkina, L. 424
 Reichinstein, D. 166, 349, 485
 Reid, E. E. 499
 Reiner, S. 384, 386
 Reiner, S., and Wlček, 386
 Reitsstötter, J. (see *Bräuer, A.*)
 Remy 330
 Reyckler, A. 86, 118, 119, 381, 386
 Reyerson, L. H., and Kobe, K. 69
 Reyerson, L. H., and Swearingen, L. E. 181
 Rhead, T. F. E., and Wheeler, R. V. 10, 122, 123
 Rheinboldt, H. (see *Wedekind, E.*)
 Rice, M. J. (see *Pearce, J. N.*)
 Richards, E. S. (see *Masson, O.*)
 Richards, T. W., and Rogers, E. F. 209
 Richardson, L. B. 11, 13, 18, 20, 30, 32, 114, 116, 117, 429, 452, 454, 473, 478, 488

- Richardson, L. B., and Woodhouse, J. C. 160, 163
 Richardson, O. W. 48, 264, 265
 Richardson, O. W., Nicol, J., and Parnell, T. 264, 266
 Rideal, E. K. 92, 423, 496, 509 ;
 (see *Bowden, F. P.* ; *Cary, A.* ;
 Hoover, G. I. ; *Hurst, W. W.* ;
 Ward, A. F. H. ; *Wilkins, F. J.*)
 Rideal, E. K., and Taylor, H. S. 499
 Rideal, E. K., and Wright, W. M. 121, 123, 509
 Riess, P. T. 250
 Rimrott, E. (see *Ruff, O.*)
 Rinne, F. 167
 Rinse, J. 236, 327
 Risler, J. 217
 Ritchie, A. D. 387
 Ritter (see *Simon, F.*)
 Roberts, J. K. 465
 Röchling, C. (see *Hofmann, K. A.*)
 Rodewald, H. 395
 Rodt, O. 387
 Roell, E. (see *Sieverts, A.*)
 Roesner, G. (see *Ruff, O.*)
 Roga, B. (see *Swientoslawski, W.*)
 Rogers, A. F. 179
 Rogers, E. F. (see *Richards, T. W.*)
 Roozeboom, B. 296, 297
 Rosanow, B. (see *Ilin, B.*)
 Rosenhain, W., and Barr, G. 387
 Rosenhain, W., Barr, G., and Booth, H. 387
 Rosenzweig, A. 371, 381
 Roth, H. (see *Magnus, A.*)
 Roth, H. E. 159
 Rother, F. 284
 Rowe, H. 38, 39, 117
 Rubenstein, L. 372, 375
 Rudberg, E. G. (see *von Euler, H.*)
 Ruff, O. 66, 67, 72, 73, 91, 481
 Ruff, O., and Backe, H. 66
 Ruff, O., and Hohlfeld, E. 66, 76, 119
 Ruff, O., Mugdan, S., Hohlfeld, E., and Feige, F. 59, 76
 Ruff, O., Rimrott, E., and Zeumer, H. 72
 Ruff, O., and Roesner, G. 64, 73, 81, 119, 157
 Ruff, O., Schmidt, G., and Olbrich, W. 67
 Ruhemann, M. (see *Simon, F.*)
 Rupp, E. 321, 322
 Rupp, E., and Schmid, E. 322
 Russell, W. W., and Taylor, H. S. 311
 Rutherford, E. 159
 Ryder, H. M. 265
 Ryland, H. S. 221
 Sabalitschka, T. 293
 Sabalitschka, T., and Moses, W. 293
 Sachs, W. (see *Frcundlich, H.*)
 Sacklowski, A. (see *Krüger, F.*)
 St. John, A. (see *Chancy, N. K.*)
 Sallinger, H. 5, 330
 Sameshima, J. 52, 83, 118, 173
 Sameshima, J., and Hayashi, K. 83, 85
 Sapozhnikov, A. V., Okatov, A. P., and Susarov, M. A. 196
 Satoh, S. 260
 Satterly, J. 157
 de Saussure, T. 2, 3, 54, 60, 65, 84, 447, 449
 Sauter, E. 499 ; (see *Magnus, A.*)
 Saxton, B. (see *Foote, H. W.*)
 Schaposchnikoff, W. G. 371, 381
 Scheele, C. W. 1
 Scheiber, J. 360
 Schelte, F. 241, 338, 339
 Scheringa 213
 Scheringa, K. 65, 144, 246
 Scherrer, P. (see *Debye, P.*)
 Scheumann, K. H. 167, 172, 174
 Scheurer, A. 371, 378, 379
 Schieferdecker, W. (see *Gutbier, A.*)
 Schilow, N. (see *Shilov*)

- Schirmann, M. A. 10, 292, 394
 Schleiermacher, A. 349
 Schlenk, W., and Weichselfelder, T. 315
 Schloesing, T., Jr. 371, 378, 379
 Schmid, E. (see *Rupp, E.*)
 Schmidt, G. (see *Ruff, O.*)
 Schmidt, G. C. 485
 Schmidt, G. C., and Durau, F. 241, 337, 338
 Schmidt, G. C., and Hinteler, B. 138, 154
 Schmidt, O. 13, 55, 56, 119, 169, 170, 173, 174, 310, 314, 315, 316, 321, 384; (see *Berl, E.*)
 Schmidt, R. (see *Gehlhoff, G.; Valentiner, S.*)
 Schneider, J. (see *Tammann, G.*)
 Schönbein 498
 Schönbein, C. F. 120
 Schroeder, H. 54
 Schulze, G. 392
 Schultze, K. (see *Ehrenberg, P.*)
 Schumacher, E. E. 276; (see *Harris, J. E.*)
 Schumacher, E. E., and Ferguson, I. 386, 387
 Schuster, C. (see *Kälberer, H. Kälberer, W.*)
 Schutzenberger, P. 209
 Schwab, G. M. 499
 Schwab, G. M., and Pietsch, E. 500, 507
 Schwabe, K. (see *Müller, E.*)
 Schwalbe, C. G. 363
 Schwalbe, C. G., and Becker, E. 371
 Schwalbe, G. 423
 Schwarz, R., and Stöwener, F. 191
 Schweitzer, J. (see *Simon, F.*)
 Scoles, S. R. 215
 Seeliger, R. 23, 172, 174
 Seeliger, R., and Lapkamp, K. 172
 Seidenberg, A. 179
 Selvig, W. A., and Kaplan, B. B. 154
 Semenoff, N. 483, 495; (see *Chariton, J.*)
 Sementschenko, W. 493
 Sessions, R. F. 59, 93, 134, 135, 148, 525
 Sever, W. (see *Bangham, D. H.*)
 Sexl, T. 482
 Shah, M. S. 9, 121, 122, 123, 124, 125, 164
 Shakespear, G. A. 28, 387; (see *Daynes, H. A.*)
 Shakespear, G. A., and Daynes, H. A. 387
 Shakespear, G. A., Daynes H. A., and Lambourn, L. J. 387
 Sharkov, V. I. (see *Nikitin, N. I.*)
 Shatunovska, H. (see *Shilov, N.*)
 Sheinker, N. S. 338
 Sheldon, H. H. 52, 59, 103
 Sheppard, S. E. 340, 362
 Sheppard, S. E., and Newsome, P. T. 362, 363, 364
 Shereshefsky, J. L. 444
 Sherman, A. (see *Taylor, H. S.*)
 Sherwood, R. G. 215, 219
 Shields, J. (see *Mond, L.*)
 Shiels, D. O. 119, 156, 236, 241, 282, 283; (see *Allmand, A. J.; Hand, P. G. T.*)
 Shilov, N. 121
 Shilov, N., and Chmutov, K. 121
 Shilov, N., Dubinin, M., and Toropov, S. 181
 Shilov, N., Shatunovska, H., and Chmutov, K. 69, 480
 Shilov, N. A., Lepin, L. K., and Voznesenskii, S. A. 25
 Shorter, S. A. 381 (see *Davidson, G. F.*)
 Shorter, S. A., and Hall, W. J. 378, 379, 381
 Shorter, S. A., Hirst, H. R., and Hall, W. J. 381
 Shrader, J. E. 215
 Siebel, K. 393
 Sieg, B. (see *von Wartenberg, H.*)

- Sieverts, A. 8, 260, 261, 262, 263, 265, 286, 288, 289, 290, 293, 298, 303, 307, 308, 316, 320, 396, 399; (see *Hagen, H.*; *Huber, H.*; *Kirschfeld, L.*)
- Sieverts, A., and Bergner, E. 213, 259, 260, 265, 266, 293
- Sieverts, A., and Gotta, A., 260, 295
- Sieverts, A., and Hagenacker, J. 261, 266, 316
- Sieverts, A., and Jurisch, E. 261, 266, 281, 285
- Sieverts, A., Jurisch, E., and Metz, A. 261
- Sieverts, A., and Krüll, F. 261
- Sieverts, A., and Krumbhaar, W. 261, 265, 266, 317
- Sieverts, A., and Müller-Goldegg, G. 261, 293
- Sieverts, A., and Roell, E. 261, 293
- Silbermann 382
- Silbermann, J. T. (see *Favre, P. A.*)
- Simon, A. 186
- Simon F. 28, 400; (see *Aharoni, J.*)
- Simon, F. (with Schweitzer, J., Glatzel, G., and Blüh, O.) 174
- Simon, F. (with Schweitzer, J., Glatzel, G., Blüh, O., Aharoni, J., Ruhemann, M., and Miss Ritter) 174
- Sirks (see *Aronstein*)
- Sissingh, R. (see *Haak, J. J.*; *Reeser, C. A.*)
- Skey, W. 93
- Skinner, C. A. 266
- Slater, F. P. 371
- Smekal, A. 329, 356, 507
- Smith (see *Gibbons*)
- Smith, C. J. (see *Rankine, A. O.*)
- Smith, D. F. (see *Loomis, A. G.*)
- Smith, D. P. 259, 286, 287; (see *Harding, E. A.*)
- Smith, H. E. (see *Frazer, J. C. W.*)
- Smith, H. G. 61; (see *McBain, J. W.*)
- Smith, J. W. 305, 306
- Smith, L. E. (see *McBain, J. W.*)
- Smith, R. A. 9, 94, 136, 160, 495
- Smith, R. F. 76
- Smits, A. 235, 392
- Smits, A., and Purcell, R. 235
- Smyth, C. P. 512
- Sogani, C. M. 80
- Sommer, H. 381, 382
- Speakman, J. B. 377, 379, 381, 396; (see *Ewles, J.*; *Whytlaw-Gray, R.*)
- Speakman, J. B., and Hirst, M. C. 382
- van der Spek, Jac. (see *Kruyt, H. R.*)
- Spence, H. S. 393
- Spencer, L. (see *Coward, H. F.*)
- Sponsler, O. L. 360, 376
- Sponsler, O. L., and Dore, W. H. 360
- Srikantan, B. S. 269
- Stacey, A. E. 381
- Stadnikov, G. L. 377
- Stafford, J. (see *Bangham D. H.*)
- Stamberger, P. 386
- Stamm, A. J. 370
- Stanford, E. C. C. 3
- Stark, N. (see *Blüh, O.*)
- Stark, N., and Blüh, O. 514
- Staud, C. J. (see *Gray, H. LeB.*)
- Steacie, E. W. R., and Graham, G. B. 254
- Steacie, E. W. R., and Johnson, F. M. G. 265, 266
- Steinhoff, E. (see *Weigel, O.*)
- Steinitzer, F. 386
- Stenhouse, J. 3, 58, 118
- Stern, O. 482; (see *Estermann, J.*)
- Steude, M. 360
- Stevenson, E. F. (see *Zsigmondy, R.*)
- Stewart, L. (see *Pease, R. N.*)
- Stimson, J. C. (see *Finch, G. I.*)

- Stock, A., Gomolka, F., and Heynemann, H. 306
 Stock, A., and Heynemann, H. 213
 Stockdale, J. (see *Evans, U. R.*)
 Stoklossa, G. 172
 Stolze 382
 Strachan, J. 360
 Stranski, I. N. 507
 Street, A. (see *Astbury, W. T.*)
 Street, J. N. (see *Morris, V. N.*)
 Streintz, F. (see *Neumann, G.*)
 Strohacker, J. 277
 Strömberg, R. 23, 223, 230, 276, 277, 305, 331
 Stöwener, F. (see *Schwarz, R.*)
 Suhrmann, R. 323
 Sullivan, R. W. (see *Holmes, H. N.*)
 Susarov, M. A. (see *Sapozhnikov, A. V.*)
 Swamy, M. V. N. (see *Venkataramaiah, Y.*)
 Swan, E. 376 ; (see *Farrow, F. D.*)
 Swan, E., and Urquhart, A. R. 485
 Swearingen, L. E. (see *Reyerson, L. H.*)
 Sweetzer, S. P. (see *Langmuir, I.*)
 Swiderek, M. 71
 Swientoslawski, W., and Chorazy, M. 71
 Swientoslawski, W., and Roga, B. 71
 Swinton, A. A. C. 217, 218
 Szegoe, L. (see *Cambi, L.*)
 von Szélényi, G. (see *von Putnok, L.*)
 Tait, P. G., and Dewar, J. 10
 Takamine, J. (see *Mills, E. J.*)
 Tamamushi, B. 525, 526
 Tammann, G. 66, 167, 168, 171, 174, 191, 233, 301
 Tammann, G., and Bochow, K. 384, 386
 Tammann, G., and Diekmann, H. 276
 Tammann, G., and Schneider, J. 291, 292, 301
 Tanner, H. G. (see *McBain, J. W.*)
 Tarassoff, W. 526
 Tarlé, M. 52
 Taylor, A. L. (see *Pearce, J. N.*)
 Taylor, G. B., Kistiakowsky, G. B., and Perry, J. H. 280, 423
 Taylor, H. S. 43, 44, 311, 422, 470, 471, 499, 500, 503, 504, 505, 506, 507, 523 ; (see *Beebe, R. A. ; Dew, W. A. ; Gauger, A. W. ; Kistiakowsky, G. B. ; Rideal, E. K. ; Russell, W. W.*)
 Taylor, H. S., and Burns, R. M. 279, 282, 308, 311, 317, 320
 Taylor, H. S., and Kistiakowsky, G. B. 208, 422, 423, 500
 Taylor, H. S., and Neville, H. A. 114
 Taylor, H. S., Neville, H. A., and Burns, R. M. 118
 Taylor, H. S., and Sherman, A. 43, 270, 471
 Taylor, H. S., and Williamson, A. T. 43, 471
 Teague, M. C. (see *Fieldner, A. C.*)
 Terry, H. I. 387
 Terwen, J. W. 310, 314
 Terzaghi, C. 350
 Theodosiu, C. N. (see *Longinescu, G. G.*)
 Thiel, A., and Hammerschmidt, W. 281
 Thiele, H. (see *Hempel, W. ; Kautsky, H.*)
 Thirrmann, W. (see *Paneth, F.*)
 Thoma, M. 292, 397
 Thomas, J. (see *Barr, G.*)
 Thomson, G. (see *Mills, E. J.*)
 Thomson, G. P. 323
 Thomson, W. 432
 Thoulet, J. 330
 Tideswell, F. V., and Wheeler, R. V. 122
 Tietze, P. 337

- Titani, T. 83
 Titoff, A. 11, 18, 19, 33, 34, 55, 86,
 95, 96, 97, 98, 114, 137, 347, 407,
 408, 409, 429, 452, 454, 455, 473,
 477, 484, 488
 Tollens, B. 213
 Topley, B. 507
 Toriyama, Y. 371; (see *Kujirai*,
T.)
 Toropov, S. (see *Shilov*, N.)
 Traube, J., and Birutowitsch, St.
 138, 200
 Traube, J., and Nishizawa, K. 339,
 340
 Travers, M. W. 6, 29, 96, 116,
 378
 Travers, M. W., Hockin, L. E.,
 and Pearce, T. J. P. 213
 Trillat, J. J. 348, 360
 Trogus, C. (see *Hess*, K.)
 Trömel, G. (see *Eitel*, W.)
 Trommsdorf 289
 Troost, L., and Hautefeuille, P.
 296, 308
 Trotman, E. R. (see *Trotman*,
S. R.)
 Trotman, S. R., and Trotman,
 E. R. 381
 Trotman, S. R., and Wyche, C. R.
 381
 Trouton, F. T. 219, 223, 328
 Trouton, F. T., and Pool, B. 125,
 378
 Trowbridge, J. 223
 Tryhorn, F. G., and Wyatt, W. F.
 52, 139, 144, 154, 164, 165
 Tschermak, G. 168, 186
 Tschischewski, N. 396
 Tschmutow, K. (see *Chmutov*)
 Turner, A. J. 371
 Ulrey, D. 216
 Urbain, E. 140
 Urelus, N. (see *Ising*, G.)
 Urquhart, A. R. 184, 365, 371;
 (see *Swan*, E.)
 Urquhart, A. R., and Eckersall, N.
 371
 Urquhart, A. R., and Williams,
 A. M. 365, 368, 370, 371
 Usher, F. L. (see *Gaunt*, H.)
 Vacher, H. C. (see *Davis*, C. W.)
 Valentiner, S. 233
 Valentiner, S., and Schmidt, R.
 157, 307
 Vanzetti, B. L. 186
 Vater, G. (see *Hempel*, W.)
 Vavon, G., and Husson, A. 504
 Venable, C. S., and Fuwa, T. 386
 Venkataramaiah, Y. 267
 Venkataramaiah, Y., and Swamy,
 M. V. N. 267
 Vignon and Bay 382
 Villars, D. S. (see *Langmuir*, I.)
 Violette, H. 65, 66, 70, 84, 144
 Volmer, M. 353, 355, 356, 486, 493,
 504; (see *Gross*, R.; *Landt*, E.)
 Volmer, M., and Adhikari, G. 236,
 353, 354
 Volmer, M., and Estermann, J.
 352, 465
 Volmer, M., and Mahnert, P. 275,
 330, 353
 Vorwerk, W. (see *Paneth*, F.)
 Voznesenskii, S. A. (see *Shilov*,
 N. A.)
 Vytopil, Z. 76
 van der Waals 451, 495
 Wachendorff, E. (see *Berl*, E.)
 Waidele, E. 54, 220
 Walker, J. (see *Carnelley*, T.)
 Walker, J., and Appleyard, J. R. 4
 Walton, R. P. 376
 Warburg, E. (see *Kundt*, A.;
Mehlhorn, F.)
 Warburg, E., and Ihmori, T. 23,
 212, 222, 253, 276, 331
 Warburg, O. 121
 Warburg, O., and Brefeld, W. 509
 Warburg, O., and Negelein, E. 121

- Ward, A. F. H. (see *Wilkins, F. J.*)
 Ward, A. F. H., and Rideal, E. K.
 86, 123, 347, 419, 496
 Ward, H. (see *Goucher, F. S.*)
 Warren, B. 386
 von Wartenberg, H., and Sieg, B.
 10
 Washburn, E. W. 90, 422
 Washburn, E. W., Footitt, F. F.,
 and Bunting, E. N. 215
 Waters, R. N. (see *Wineland, A. J.*)
 Watson, F. S. (see *Firth, J. B.*)
 Watson, H. E. 65
 Watson, H. E., and Menon, A. S.
 350
 Weber, H. (see *Meyerhof, O.*)
 Weber, L. I., and Lewin, G. 349
 Wedekind, E. 481
 Wedekind, E., and Rheinboldt, H.
 481
 Wedekind, E., and Wilke, H. 481
 Weichselfelder, T. (see *Schlenk, W.*)
 Weide, H. F. (see *Holmes, H. N.*)
 Weigel, O., and Steinhoff, E. 23,
 169, 173
 Weil, K. (see *Peters, K.*)
 von Weimarn, P. P. 360
 Weise, G. L. (see *Gutbier, A.*)
 Weiser, H. B. 180
 Welke, K. (see *Polányi, M.*)
 Welo, L. A. 260
 Welo, L. A., and Baudisch, O. 202
 Wheeler, R. V. 122 ; (see *Francis, W. ; Rhead, T. F. E. ; Tidswell, F. V.*)
 White, A. (see *Frolich, K.*)
 White, A. M. 22
 White, T. A. (see *Benton, A. F.*)
 Whitehouse, A. G. R. 419
 Whytlaw-Gray, R., Speakman, J. B., and Campbell, J. H. P.
 273
 Wibaut, J. P. 72
 Wiedbrauck, E. (see *Lorenz, R.*)
 Wiedemann, G. 251
 Wiegand, W. B., and Boggs, C. R.
 144
 Wilke, H. (see *Wedekind, E.*)
 Wilkins, F. J. 319, 343, 355
 Wilkins, F. J., and Rideal, E. K.
 318
 Wilkins, F. J., and Ward, A. F. H.
 482, 487
 Will, W. 362
 Willavoy, H. J. 372, 374, 375
 Williams, A. M. 31, 32, 41, 86, 87,
 88, 119, 346, 349, 416, 428, 430,
 447, 485, 489, 490, 491, 493 ;
 (see *Urquhart, A. R.*)
 Williams, G. A., and Ferguson, J. B. 213
 Williams, I., and Neal, A. M. 386
 Williams, J. W. 512
 Williams, R. R., and Murphy, E. J. 371
 Williamson, A. T. (see *Taylor, H. S.*)
 Willows, R. S. 215
 Willows, R. S., and George, H. T.
 218
 Willstätter, R., and Kraut, H. 186
 Willstätter, R., Kraut, H., and
 Erbacher, O. 186
 Willstätter, R., Kraut, H., and
 Fremery, W. 186
 Willstätter, R., Kraut, H., and
 Lobinger, K. 186
 Wilson, R. E. 103, 438 ; (see *Lamb, A. B.*)
 Wilson, R. E., and Fuwa, T. 154,
 387
 Wineland, A. J., and Waters, R. N. 387
 Winkler, J. (see *Burstin, H.*)
 Winter, R. M., and Baker, H. B.
 60, 91
 Witt, R. K. (see *Andrews, D. H.*)
 Wlček 385 ; (see *Reiner, S.*)
 Woker, G. 499
 Wolf, G. 8, 292, 398, 399

- Wolfenden, J. H. 315
Wolff, H. 241, 337
Woo, L. P. L. (see *Klosky, S.*)
Wood, F. C. (see *Coward, H. F.*)
Wood, R. W. 465, 505
Woodhouse, J. C. 146; (see *Richardson, L. B.*)
Woodmansey, A. 378
Woods, H. J. (see *Astbury, W. T.*)
Woog, P. 355
Workman, O. (see *Philip, J. C.*)
Wright, A. M. 378
Wright, R. H., and Marshall, M. J. 25
Wright, W. M. (see *Rideal, E. K.*)
von Wroblewski, S. 262, 265, 384, 386
Wulff, J. 23, 237, 258, 307, 485
Wyatt, W. F. (see *Tryhorn, F. G.*)
Wyche, C. R. (see *Trotman, S. R.*)
Wykoff, W. G. 67
Yamada, M. 302, 398
Yamamoto, T. 386
Yoshikawa, K. (see *Kubota, B.*)
Young, F. B. 28
Yuryev, V. I. (see *Nikitin, N. I.*)
Zeise, H. 18, 21, 40, 243, 244, 279, 346, 473, 477, 478, 486, 487, 488, 489
Zelinsky, N. D., and Rakusin, M. A. 28, 154, 156
Zenghelis, C. 213
Zeumer, H. (see *Ruff, O.*)
Zhukov, I. I. 284, 285, 289
Zies, E. G. (see *Allen, E. T.*)
Zimmerlund, G. (see *von Euler, H.*)
Zocher, H. (see *Kautsky, H.*)
Zsigmondy, R. 159, 177, 181, 182, 184, 365, 393, 395, 432, 433, 434, 439, 441
Zsigmondy, R., Bachmann, W., and Stevenson, E. F. 184
Zulkowsky 386
Zwicky, F. 329, 507
Zwikker, C. (see *de Boer, J. H.*)

SUBSTANCE INDEX

Capitals indicate sorbing agent; ordinary type represents substances sorbed.

AGATE

iodine 201

ALGÆ, MARINE

gases, asphyxiating 14

ALUMINA

acetic acid 203, 204, 205, 393

acetone 203, 393

acetylene 200

alcohols 200, 203, 205, 208, 393

ammonia 198, 201, 203

benzene 200, 204, 393

carbon dioxide 198, 201, 203,
310

carbon disulphide 203, 204, 410

carbon disulphide and water 203

carbon tetrachloride 204, 393

chloroform 204, 393

dichlorethane 204

dichlorethylene 204

esters 203

ether 203, 393

ethyl acetate 203, 205

ethyl alcohol 203

ethylene 200

ethylene hydrocarbons 200

halogen derivatives 203

hexane 204, 393

hydrocarbons 197, 203

hydrogen 310

iodine 201

iso-butylene 200

litmus 3

methyl acetate 204

methyl ethyl ketone 204

organic compounds 203, 410

ALUMINA (*contd.*)

radium emanation 203

sulphindigodate 3

sulphur dioxide 203

thorium emanation 203

toluene 204

water 192, 194, 203, 205, 207,
410, 442

water and carbon disulphide 203

ALUMINIUM

ammonia 321

argon 260, 262, 321

carbon dioxide 321

ethane 321

ethylene 321

helium 260, 262

hydrogen 260, 262, 307, 321, 397

methane 321

nitrogen 260, 261, 262, 321

nitrous oxide 321

noble gases 307

xenon 307

ALUMINIUM SILICATE

hydrocarbons 197

AMMONIUM CHLORIDE

gases 246

water 246

AMMONIUM CHROMIUM OXALATE

water 168

ANALCITE

water 395

ANORTHITE

water 249, 250, 442

ANTIMONY

hydrogen 260, 262

- ANTIMONY (*contd.*)
 nitrogen 260, 262
 stibine 306
- ANTIMONY OXIDE
 argon 159
 litmus 3
 sulphindigodate 3
- ANTIMONY SULPHIDE
 litmus 3
 sulphindigodate 3
- ASBESTOS
 ammonia 114
 gases 2
 helium 214
 sulphur dioxide 114 283
 water 389
- BARIUM SULPHATE
 electrolytes 330
 litmus 3
 sulphindigodate 3
 thorium B 334
 thorium X 334
- BEETS
 air 377
 carbon dioxide 377
 nitrogen 377
 oxygen 377
- BENTONITES
 water 393
- BENZOPHENONE
 benzophenone 353
- BERYLLIUM OXIDE
 iodine 201
- BISMUTH
 hydrogen 260, 262, 287
 nitrogen 260, 262
- BISMUTH AND ZINC
 methyl alcohol 395
 water 395
- BISMUTH TRISULPHIDE
 acetone 334
 dyes 334
 sodium brucine sulphonate 334
- BREAD (WHITE)
 water 388
- BRICKS
 water 211
- BUILDING MATERIALS
 water 390, 406
- CADMIUM
 hydrogen 260, 262, 287, 307
 methyl alcohol 395
 nitrogen 260, 262
 water 395
- CALCIUM
 argon 159
- CALCIUM CARBONATE
 acetic acid 393
 acetone 393
 alcohol 393
 benzene 393
 carbon tetrachloride 393
 chloroform 393
 ether 393
 hexane 393
- CALCIUM FLUORIDE
 iodine 258, 496
- CALCIUM OXIDE
 ammonia, 201
- CALCIUM PHOSPHATE
 litmus 3
 sulphindigodate 3
- CALCIUM SULPHATE
 thorium B 334
 thorium X 334
- CALOMEL
 litmus 3
 sulphindigodate 3
- CARBON AND SILICA (CARBO-GEL)
 ammonia 181
 benzene 181
 chlorine 181
 toluene 181
 water 181
- CARBORUNDUM
 ammonia 48
- CASSITERITE
 argon 159
- CATGUT
 water 387, 388

CELLOBIOSE

water 363

CELLULOID

ammonia 384

carbon dioxide 384

hydrogen 384

oxygen 384

sulphur dioxide 384

CELLULOSE (see *Cotton*)

CERIUM

hydrogen 261, 287, 294, 303, 304

CERIUM ALLOYS

hydrogen 261

CERIUM ALLOYED WITH MAGNESIUM

hydrogen 261

CHABASITE

acetone 169, 174

acetylene 172

air 171

ammonia 13, 172, 173

amyl alcohol 173

argon 173, 174

benzene 169, 173, 174

butadiene 173

butylamine 174

butylene 173

carbon dioxide 172, 173, 174

carbon disulphide 174

carbon monoxide 173

carbon tetrachloride 174

chloroform 174

ethane 173

ether 169, 173, 174

ethyl acetate 174

ethyl alcohol 169, 174

ethylamine 174

ethylene 173, 174

formic acid 169

helium and neon 172

hexamethylene 173

hydrogen 172, 173, 174

methane 172, 173

methyl alcohol 169, 174

methylamine 174

neon and helium 172

CHABASITE (*contd.*)

nitric oxide 172

nitrogen 172, 173, 174

oxygen 172, 173, 175

pentane 174

propylamine 174

propylene 173

water 13, 145, 146, 169, 170, 171, 173, 394

CHALK

water 211

CHARCOAL (INCLUDING COKE AND LIGNITES)

acetic acid 52, 77, 134, 136, 140, 393, 434

acetone 130, 134, 136, 138, 139, 200, 335, 393, 407; (see also *mixtures*)acetylene 52, 102, 105, 119, 408; (see also *mixtures*)

actinium emanations 159

alcohol 52, 65, 134, 136, 162, 200, 393; (see also *mixtures*)

ammonia 2, 30, 33, 47, 52, 55, 56, 64, 73, 95, 96, 102, 105, 107, 114, 115, 116, 117, 118, 119, 136, 137, 140, 181, 377, 393, 405, 407, 409, 419, 473, 477, 527

amylene 136

amyl iodide 136

amyl nitrite 138

aniline 136

argon 7, 15, 55, 56, 64, 73, 97, 99, 100, 119, 157, 158, 406, 458, 473; 492 (see also *mixtures*)

benzaldehyde 136

benzene 38, 52, 63, 65, 119, 131, 132, 133, 134, 136, 137, 138, 139, 140, 141, 143, 178, 181, 200, 345, 393, 406, 407, 408, 413, 437; (see also *mixtures*)

bromine 68, 72, 120, 138, 406

butyl alcohol 139; (see also *mixtures*)

CHARCOAL (*contd.*)

butyl chloride 125
 butyric acid 136
 butyric ether 136
 camphor 136
 carbolic acid, 136
 carbon dioxide 2, 10, 11, 12, 13,
 29, 33, 38, 52, 55, 56, 60, 62,
 64, 70, 72, 73, 81, 83, 93, 95,
 96, 97, 99, 100, 102, 103, 105,
 106, 107, 111, 114, 115, 116,
 117, 118, 119, 121, 122, 124,
 136, 137, 163, 166, 377, 390,
 391, 405, 406, 407, 408, 409,
 417, 419, 449, 454, 455, 456,
 457, 458, 473, 477, 478, 491,
 492, 514; (see also *mixtures*)
 carbon disulphide 52, 110, 126,
 127, 136, 137, 138, 139, 141,
 200, 203, 345, 407, 408, 410,
 415, 437, 439, 452
 carbon monoxide 38, 39, 55, 56,
 70, 78, 97, 99, 100, 102, 105,
 107, 119, 122, 124, 136, 161,
 162, 406, 408, 458, 492; (see
 also *mixtures*)
 carbon tetrachloride 52, 73, 74,
 93, 94, 125, 132, 134, 137, 138,
 139, 164, 178, 345, 393, 401,
 407, 408
 carbonic anhydride 136
 carbonic oxide 2
 carbonyl chloride 102, 141
 cæsium nitrate 424
 chlorine 25, 72, 102, 119, 120,
 140, 181, 406, 419
 chloroform 52, 125, 136, 137,
 138, 163, 345, 393, 401, 407,
 408, 493; (see also *mixtures*)
 chloropicrin 47, 68, 74, 140,
 419
 colouring matter 2
 crystal violet 424
 cyanogen 105, 107, 119, 136
 decane 94, 139
 ethane 56, 105, 119, 408; (see

CHARCOAL (*contd.*)

also *mixtures*)
 ether 52, 119, 134, 136, 137, 138,
 139, 200, 393, 407, 408, 413,
 437
 ethyl acetate 136, 138, 200
 ethyl alcohol 134, 138, 140, 141,
 200, 408; (see also *mixtures*)
 ethyl bromide 408
 ethyl carbonate 345
 ethyl chloride 125, 126, 127, 138,
 407, 408, 412
 ethyl formate 137, 138, 408
 ethyl iodide 136, 408
 ethyl propionate 52
 ethylamine 136
 ethylene 2, 31, 55, 56, 97, 99,
 100, 105, 109, 110, 111, 113,
 119, 408, 458, 475, 492; (see
 also *mixtures*)
 formaldehyde 136
 formic acid 136
 fousel oil 136
 "gases" 1, 2
 gases, asphyxiating 14
 helium 10, 43, 97, 135, 143, 156,
 157, 406
 hexachlorethane 136
 hexane 94, 138, 200, 393
 hydrocarbons, aromatic 130
 hydrocarbons, normal straight
 chain 139
 hydrocarbons, saturated 130
 hydrochloric acid 2, 102, 118,
 119, 121, 377, 407
 hydrochloric ether 136
 hydrogen 2, 6, 8, 33, 34, 37, 38,
 39, 42, 43, 47, 52, 55, 56, 69,
 70, 79, 83, 93, 95, 96, 97, 98,
 102, 103, 107, 108, 109, 113,
 114, 119, 121, 135, 136, 157,
 162, 163, 179, 269, 377, 406,
 458; (see also *mixtures*)
 hydrogen bromide 407
 hydrogen iodide 407
 hydrogen sulphide 2, 102

CHARCOAL (*contd.*)

iodine 8, 46, 48, 65, 77, 93, 120, 178, 201; (see also *mixtures*)
 iso-amyl alcohol 138, 200, 407
 krypton 157, 158
 lead nitrate 335
 lithium nitrate 424
 litmus 3
 mercury 27, 28, 154, 155, 156, 416
 methane 55, 56, 97, 99, 100, 102, 107, 113, 119, 125, 136, 401, 458, 478, 492; (see also *mixtures*)
 methanol 137
 methyl acetate 136, 137, 138, 200
 methyl alcohol 130, 131, 134, 136, 138, 140, 200, 407, 408; (see also *mixtures*)
 methyl benzoate 52, 139
 methyl chloride 102, 125, 401, 405, 407
 methyl ethyl ketone 138, 200
 methyl green 335
 methylamine 55, 140
 methylene blue 65, 75, 77
 methylene blue B extra 335
 methylene chloride 125, 401, 407
 mixtures 99, 161
 acetone and benzene 164, 165
 acetylene and hydrogen 162
 air 47, 48, 51, 83, 84, 85, 103, 107, 114, 119, 121, 136, 160, 161, 162, 193, 377, 393, 405
 air, hydrogen and carbon dioxide 165
 alcohol and benzene 164
 argon and nitrogen 119
 benzene and acetone 164, 165
 benzene and alcohol 164
 benzene and butyl alcohol 165
 benzene and ethyl alcohol 165
 benzene and iodine 162
 benzene and methyl alcohol 165

CHARCOAL (*contd.*)

benzene and propyl alcohol 165
 benzene and water 178
 butyl alcohol and benzene 165
 carbon dioxide and carbon monoxide 166
 carbon dioxide and ethylene 166
 carbon dioxide and hydrogen 162, 166
 carbon dioxide, hydrogen and air 165
 carbon dioxide, nitrogen, oxygen and hydrogen 25, 161
 carbon dioxide and nitrous oxide 163, 164
 carbon monoxide and carbon dioxide 166
 carbon monoxide and nitrogen 97, 162
 carbon monoxide and oxygen 162, 406
 chloroform and sulphur dioxide 163
 ethane and hydrogen 162
 ethyl alcohol and benzene 165
 ethylene and carbon dioxide 166
 ethylene and hydrogen 162
 ethylene, methane and nitrogen 161
 ethylene and nitrogen 162, 163
 hydrogen and acetylene 162
 hydrogen and carbon dioxide 162, 166
 hydrogen, carbon dioxide and air 165
 hydrogen and ethane 162
 hydrogen and ethylene 162
 hydrogen and methane 113, 162
 hydrogen and oxygen 97, 162, 406

CHARCOAL (*contd.*)

hydrogen and nitrogen 163
hydrogen, oxygen, nitrogen
and carbon dioxide 25, 161
hydrogen and sulphur dioxide
163
iodine and benzene 162
methane, ethylene and nitro-
gen 161
methane and hydrogen 113,
162
methyl alcohol and benzene
165
nitrogen and argon 119
nitrogen and carbon monoxide
97, 162
nitrogen and ethylene 162,
163
nitrogen and hydrogen 163
nitrogen, methane and ethyl-
ene 161
nitrogen and oxygen 104, 160,
161, 162, 163, 164
nitrogen, oxygen, hydrogen
and carbon dioxide 25, 161
nitrous oxide and carbon
dioxide 163, 164
oxygen and carbon monoxide
162, 406
oxygen and hydrogen 97, 162,
406
oxygen, hydrogen, nitrogen
and carbon dioxide 25, 161
oxygen and nitrogen 104, 160,
161, 162, 163, 164
propyl alcohol and benzene
165
sulphur dioxide and chloro-
form 163
sulphur dioxide and hydrogen
163
water and benzene 178
naphthaline 136
neon 156, 157
nitric oxide 124, 125, 418
nitrobenzol 136

CHARCOAL (*contd.*)

nitrogen 2, 9, 14, 37, 38, 39, 42,
52, 55, 56, 68, 70, 79, 91, 93,
94, 95, 96, 97, 99, 100, 101,
102, 103, 104, 105, 108, 109,
112, 113, 119, 121, 124, 135,
136, 157, 162, 163, 179, 193,
377, 406, 407, 408, 430, 438,
440, 458, 459, 460, 473, 476,
478, 492, 493, 497; (see also
mixtures)
nitrous ether 136
nitrous oxide 2, 94, 102, 104,
105, 109, 110, 111, 112, 113,
119, 124, 136, 163, 407, 408,
440, 474; (see also *mixtures*)
noble gases 156, 193
non-polar compounds 130
octane 129, 130
organic compounds 148, 149,
178, 203, 410, 424
oxalic acid 65
oxalic ether 136
oxygen 2, 3, 8, 9, 38, 42, 53, 55,
59, 69, 70, 93, 94, 95, 97, 99,
100, 102, 103, 104, 108, 120,
121, 123, 124, 135, 136, 161,
162, 163, 193, 278, 377, 406,
407, 417, 418, 419, 420, 421,
428, 438, 440, 458, 480, 481;
(see also *mixtures*)
pentane 138, 139, 414
phenol 59, 60, 62, 77
polar molecules 130
Ponceau 2R 335
potassium nitrate 424
propyl alcohol 138, 200, 407,
439; (see also *mixtures*)
propyl chloride 125, 407
quinine 77
quinine sulphate 65
radioactive emanations 156
radium emanations 159, 193
salicyl hydride 136
salicylic acid 136
strychnine 4

CHARCOAL (*contd.*)

- succinic acid 51
- sulphindigodate 3
- sulphur 72
- sulphur dioxide 39, 60, 81, 102, 105, 114, 115, 117, 119, 136, 163, 377, 407, 408, 416, 527; (see also *mixtures*)
- sulphurous acid 2
- tartar emetic 65
- thorium emanations 159
- toluene 34, 35, 52, 66, 128, 130, 139, 140, 148, 149, 434
- triethylamine 136
- turpentine, oil of 136
- valerianic acid 136
- water 39, 47, 52, 65, 66, 136, 137, 138, 139, 140, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 162, 178, 181, 192, 193, 200, 203, 343, 344, 387, 389, 391, 410, 415, 416, 419, 425, 430, 437, 441, 442, 446, 525; (see also *mixtures*)
- xenon 157, 158

CHARCOAL AND GLASS

- ammonia 107
- carbon dioxide, 107

CHROMIC OXIDE

- ammonia 198, 201, 202
- carbon dioxide 198
- water 192, 194

CHROMIC OXIDE AND ZINC OXIDE

- hydrogen 208, 411

CHROMIUM

- hydrogen 287

CHROMIUM CHLORIDE

- water 246

CHROMIUM OXIDES

- carbon monoxide 10
- hydrogen 10

CLAY

- hydrocarbons 197

COAL

- air 107, 377

COAL (*contd.*)

- carbon dioxide 85, 107, 108, 377
- carbon monoxide 107
- hydrogen 79
- methane 85, 107, 108
- nitrogen 79, 85, 107, 108, 377
- oxygen 85, 107, 122, 377

COBALT

- ammonia 310
- carbon dioxide 307, 310, 311
- carbon monoxide 311
- ethylene 311
- hydrogen 260, 262, 266, 287, 307, 308, 309, 310, 311
- nitrogen 260

COBALT OXIDE

- carbon dioxide 209
- oxygen 209
- water 194

COLUMBIUM

- hydrogen, 261, 287

COPPER

- air 264
- ammonia, 310, 317, 422, 507
- argon 260, 262
- bromine 307
- carbon dioxide 260, 261, 262, 264, 307, 310, 311
- carbon monoxide 260, 261, 262, 311, 312, 317, 318, 319, 422, 504
- carbon monoxide and hydrogen 318, 319
- chlorine 307
- ethane 317, 318, 423
- ethyl sulphide 315
- ethylene 207, 311, 317, 318, 422, 504
- helium 260, 262
- hydrogen 207, 260, 261, 262, 263, 264, 266, 287, 307, 308, 309, 310, 311, 315, 317, 318, 319, 322, 399, 417, 418, 421, 422, 423, 504
- hydrogen and carbon monoxide 317, 318

COPPER (*contd.*)

- hydrogen sulphide 307, 315
- iodine 307
- nitric acid 307
- nitrogen 260, 261, 262, 316, 317, 318
- oxygen 261, 319
- sulphur dioxide 260, 261, 262, 265
- sulphurous gases from rubber 307
- thiophene 315
- COPPER ALLOYED WITH GOLD
 - sulphur dioxide 260
- COPPER ALLOYED WITH PALLADIUM
 - carbon monoxide 318, 319
 - carbon monoxide and hydrogen 318, 319
 - hydrogen 318, 319
- COPPER ALLOYED WITH PLATINUM
 - sulphur dioxide 260
- COPPER ALLOYED WITH SILVER
 - sulphur dioxide 260
- COPPER ALLOYS
 - hydrogen 261
 - sulphur dioxide 265
- COPPER OXIDE
 - carbon dioxide 209, 500
 - carbon monoxide 10, 209
 - hydrogen 10, 209
 - litmus 3
 - oxygen 209
 - sulphindigodate, 3
 - water 192, 194, 210, 441, 442, 443
- COPPER OXIDE AND MANGANESE DIOXIDE
 - water 441
- COPPER, OXYGEN AND SULPHUR COMPOUNDS OF
 - sulphur dioxide 260
- COPPER SULPHATE
 - water 194
- COPPER SULPHIDE (COPPER
• PYRITES)
 - oleic acid 496

CORK

- air 377
- carbon dioxide 377
- nitrogen 377
- oxygen 377

COTTON

- acetic acid, glacial 369, 370
- acetone 369, 370
- alcohol, absolute 369, 370
- ammonia 378
- benzene 369, 370
- carbon dioxide 72
- carbon disulphide 369, 370
- ether 369, 370
- fogs 358
- gases, asphyxiating 14
- nitrobenzene 369, 370
- smokes 358
- water 364, 365, 366, 367, 368, 369, 370, 378, 379, 380, 381, 382, 387, 388

CRACKERS

- water 388

DIAMOND

- methyl green 334, 335
- methylene blue 15, 334, 335
- succinic acid 15

FEATHERS

- water 387, 388

FERRIC HYDROXIDE

- acetic acid 393
- acetone 204, 393
- alcohol 204, 393
- ammonia 198, 201, 202, 204
- benzene 178, 190, 191, 204, 393
- butyl alcohol 204
- carbon dioxide 198, 202, 209
- carbon disulphide 203
- carbon disulphide and water 203
- carbon monoxide 206, 209
- carbon tetrachloride 204, 393
- chloroform 204, 393
- dichlorethylene 204
- ether 393

FERRIC HYDROXIDE (*contd.*)

- ethyl bromide 204
- ethylene 207
- gasoline 204
- hexane 393
- hydrogen 207, 209
- iso-butyl alcohol 204
- litmus 3
- methyl alcohol 204
- methyl iodide 204
- oxygen 202, 209
- radium emanation 203
- sulphindigodate 3
- sulphur dioxide 204
- thorium emanation 203
- water 178, 192, 194, 202, 203, 387, 389
- water and carbon disulphide 203

FERRIC OXIDE; (see *Ferric hydroxide*)**FEROUS SULPHIDE**

- sulphur 242
- " FILTER CEL "
- water 211

FILTER PAPER

- sodium chloride 360
- sodium tungstate 360
- water 378, 388

FIUGGI TUBA

- carbon dioxide 159
- helium 159
- oxygen 159

FLAX (see *Linen*)**FLORIDIN**

- acetylene 200
- alcohol 200
- benzene 200
- carbon disulphide 203, 410
- ethylene 200
- iso-butylene 200
- organic compounds 203, 410
- water 203, 410

FLOUR

- water 388

FOODSTUFFS

- water 387

FULLER'S EARTH

- acetic acid 393
- acetone 393, 437
- alcohol 393
- benzene 393, 437
- carbon tetrachloride 393
- chloroform 393
- ether 393
- hexane 393
- water 194, 387, 389

GALENA

- methylene blue 354

GELATINE

- ammonia 384
- benzene 193
- carbon dioxide 384
- hydrogen 384
- oxygen 384
- sulphur dioxide 384
- water 192, 193, 388

GERMANIUM

- hydrogen 261

GLASS

- acetone 232
- acetonitrile 234
- acetylene 200, 236, 239, 241
- air 216, 234, 240, 242, 243
- alcohol 200, 224
- ammonia 47, 48, 49, 50, 234, 236, 239, 240, 241, 243, 440
- ammonium bromide 235
- ammonium ion 328
- argon 243
- benzene 200, 224, 235
- benzophenone 236, 354
- brilliant safranin 338
- calcium ion 328
- carbon dioxide 48, 214, 215, 224, 233, 234, 236, 238, 239, 240, 241, 242, 243, 440, 449
- carbon dioxide and oxygen, 214
- carbon disulphide 237, 339
- carbon monoxide 234, 243, 469
- charcoal 233
- chloroform 224

GLASS (*contd.*)

crystal violet 336, 339
 diamond fuchsine 237, 338
 dyes 328
 ethyl violet 237, 338
 ethylene 200, 234, 243
 formaldehyde 232
 fuchsine 339
 gases 246
 gases, permanent 240
 halogens 213
 helium 213, 214
 hydrogen 40, 213, 216, 233, 234,
 235, 239, 240, 242, 244, 245,
 421, 505
 hydrogen ion 328
 iodine 235, 236
 iron 506
 iso-butylene 200
 mercuric bromide 236
 mercuric chloride 236
 mercuric iodide 236, 327
 mercurous chloride 236
 mercury 236
 metals 149, 465
 methane 40, 243, 244, 469,
 489
 methyl alcohol 232
 methyl chloride 237, 243, 339
 methyl violet 337, 338
 methyl violet BB 338
 methylene blue 338, 339
 neon 214
 nickel 506
 nitrogen 40, 213, 216, 224, 242,
 243, 244, 489
 nitrogen pentoxide 242
 nitromethane 232, 234
 nitrous oxide 48, 236, 239, 241,
 440
 noble gases 465
 oxygen 40, 214, 215, 242, 243,
 244, 489
 oxygen and carbon dioxide 214
 pentane 237, 339
 platinum 506

S.G.V.

GLASS (*contd.*)

potassium bromide 328
 potassium chloride 328
 potassium ion 328
 pyridine 233
 quinine ion 328
 sodium chloride 328
 sodium ion 328
 sulphur dioxide 48, 239, 240,
 241, 243
 toluene 224, 230, 232, 233, 234
 water 8, 145, 146, 214, 217, 219,
 221, 222, 223, 224, 225, 226,
 227, 228, 229, 230, 231, 232,
 233, 234, 239, 240, 389, 393,
 425

GLASS AND CHARCOAL

ammonia 107
 carbon dioxide 107

GLUCINUM

hydrogen 287

GLUCOSE

water 363

GLUE

water 387, 388

GOLD

air 277
 ammonium thiocyanate 332
 argon 260, 262, 267
 carbon dioxide 267
 carbon monoxide 267
 electrolytes 332
 helium 260, 262
 hydrogen 260, 262, 266, 267,
 287, 323
 hydrogen and oxygen 267
 nitrogen 260, 262, 267
 oxygen 261, 262, 266, 267
 oxygen and hydrogen 267
 potassium chloride 332
 silver nitrate 332
 silver sulphate 332
 sodium sulphate 332
 sulphuric acid 332
 toluene 306
 water 267, 276

O.O.*

GRANITE

water 211

GRAPHITE

acetic acid 393

acetone 393

alcohol 393

ammonia 118, 405

benzene 393

carbon dioxide 118, 405, 440

carbon tetrachloride 393

chloroform 393

ether 393

hexane 393

hydrogen 71, 79, 440

methylene blue 15

nitrogen 79

oxygen 48, 71, 440

succinic acid 15

water 194

GRASS

gases, asphyxiating 14

GUNCOTTON

sulphur dioxide 377

HAY

gases, asphyxiating 14

HEMOGLOBIN

carbon monoxide 78

HEMP

water 378, 381, 388

HEULANDITE

ammonia 172, 173

carbon dioxide 173

ethylene 173

water 172

HOPCALITE

carbon dioxide 209

carbon monoxide 44, 209

hydrogen 209

oxygen 209

INDIGO

litmus 3

sulphindigodate 3

INDIUM

hydrogen 261

IRIDIUM

carbon monoxide 283, 284

hydrogen 283, 284, 286, 287, 294

nitrogen 283

IRON

ammonia 310, 317, 319, 422, 507

argon 260, 262

carbon dioxide 307, 310, 311,
319, 320carbon monoxide 260, 262, 265,
311, 320

ethylene 311, 320

helium 260, 262

hydrogen 260, 261, 262, 263,
265, 266, 287, 291, 307, 308,
310, 311, 317, 319, 320, 322,
396, 397, 399, 471

litmus 3

nitrogen 260, 261, 263, 265, 266,
396, 471

oxygen 261

sulphindigodate 3

IRON ALLOYS (FERROUS)

carbon monoxide 260

hydrogen 260

nitrogen 260

IRON AND MOLYBDENUM

ammonia, 316, 317

hydrogen 316

IRON NITRIDE

hydrogen 260

JUTE

water 381, 388

KAOLIN

acetylene 200

alcohol 200

benzene 200

ethylene 200

iso-butylene 200

water 192, 194, 389

KIESELGUHR

hydrogen 102, 103

nitrogen 102, 103

water 194, 211, 389

- LANTHANUM
hydrogen 287, 293
- LANTHANUM ALLOY
hydrogen 260, 261, 303
- LEAD
ammonia, 310
carbon dioxide 310
hydrogen 260, 262, 287, 310
methyl alcohol 395
nitrogen 260, 262
water 395
- LEAD CHROMATE
litmus 3
sulphindigodate 3
- LEAD PHOSPHATE
acetone 334
dyes 334
sodium brucine sulphonate 334
- LEAD SULPHATE
acetone 334
dyes 334
litmus 3
methylen blue 336, 337
Ponceau Red 2R 42, 334
sodium brucine sulphonate 334
sulphindigodate 3
thorium B 333
- LEAD SULPHIDE
acetone 334
dyes 334
litmus 3
sodium brucine sulphonate 334
sulphindigodate 3
- LEATHER
water 387, 388
- LEAVES (FRESH)
gases, asphyxiating 14
- LIMESTONE
water 211
- LINEN
ammonia 378
water 371, 378, 379, 381, 382,
387, 388
- LITHARGE
litmus 3
sulphindigodate 3
- MACARONI
water 387, 388
- MAGNESIUM
argon 260, 262
helium 260, 262
hydrogen 287
- MAGNESIUM OXIDE
acetic acid 393
acetone 393
alcohol 393
benzene 393
carbon dioxide 500
carbon tetrachloride 393
chloroform 393
ether 393
hexane 393
iodine 201
water 194
- MANGANESE
hydrogen 287
- MANGANESE DIOXIDE
benzene 210
carbon dioxide 209, 210
carbon monoxide 209
hydrogen 209
litmus 3
nitrogen 209
oxygen 209
sulphindigodate 3
water 192, 210, 441
- MANGANESE DIOXIDE AND COPPER
OXIDE
water 441
- MANGANOUS OXIDE
water 194
- MEERSCHAUM
ammonia 405
gases 2
methyl chloride 405
sulphur dioxide 114
- MERCURY
air, 270, 271, 273
benzene 275
benzophenone 275, 330, 353, 354
bromine 307
carbon dioxide 273, 274, 330

MERCURY (*contd.*)

- cetyl alcohol 355
- chlorine 307
- coumarin 355
- diphenylmethane 355
- ethyl alcohol 275
- ethyl bromide 275
- hydrogen 271, 272, 287
- hydrogen sulphide 307
- iodine 307, 327
- mercurous chloride 331
- mercury 352
- methyl acetate 275
- methyl iodide 275
- methylene blue 337
- nitric acid 307
- oil 271
- paraffin 355
- phthalic anhydride 355
- propyl chloride 275
- water 275

MERCURY AND TIN

- methyl alcohol 395
- water 395

METASTANNIC ACID

- sulphuric acid 5

MICA

- argon 252
- carbon dioxide 252
- carbon monoxide 252
- methane 252
- nitrogen 30, 252
- oxygen 252
- water 250, 251

MOLYBDENUM

- barium 269
- carbon monoxide 285, 286
- hydrogen 286, 287, 322
- nitrogen 285, 286
- rare earth metals 269

MOLYBDENUM AND IRON

- ammonia 316, 317
- hydrogen 316

MOUNTAIN CORK

- gases 2

NEODYMIUM

- hydrogen 261, 287, 293

NICKEL

- ammonia 310, 315, 317, 422, 507
- argon 260, 262, 267
- carbon dioxide 267, 307, 310, 311, 312
- carbon monoxide 260, 261, 262, 267, 311, 399
- ethane 315, 316, 421
- ethyl sulphide 315
- ethylene 207, 311, 315, 316, 421
- helium 260, 262
- hydrogen 207, 260, 261, 262, 263, 264, 266, 267, 287, 291, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 322, 397, 398, 399, 418, 421, 471, 497, 505, 506

hydrogen and nitrogen 311

hydrogen and oxygen 267

hydrogen sulphide 315

methane 315

nitrogen 260, 262, 267, 311, 315, 471

nitrogen and hydrogen, 311

oxygen 267

oxygen and hydrogen 267

thiophene 315

water 267, 316

NICKEL AND THORIA

carbon dioxide 311

hydrogen 311

nitrogen 311

NICKEL SULPHIDE

argon 159

NITROCOTTON

acetone 372, 373, 374, 375

amyl alcohol 374

benzene 373, 374

benzyl alcohol 374

butyl acetate 374

butyl alcohol 374

carbon tetrachloride 374

chloroform 374

cyclohexanol, 374

NITROCOTTON (*contd.*)

- decane 374
- ethyl alcohol 372, 374
- hexane 374
- iso-butyl alcohol 374
- iso-propyl acetate 374
- methyl acetate 374
- methyl alcohol 373, 374, 375
- methyl ethyl ketone 372, 373, 374
- methyl phenyl urethane 374
- octyl alcohol 374
- toluene 374
- water 362

OCTAACETATE

- water 363

OPAL

- iodine 201

OSMIUM

- hydrogen 284, 285, 294

OXIDE CATALYSTS

- hydrogen 270

OXYGEN, SORBED

- nitric oxide 125
- nitrous oxide 125, 164

PALLADIUM

- air 260, 264
- argon 260, 262, 394
- carbon dioxide 264, 307, 311
- carbon monoxide 289, 311, 313
- ether 260
- ethylene 311
- helium 214, 260, 262, 283, 394
- hydrogen, 8, 259, 260, 261, 264, 267, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 307, 311, 313, 394, 396, 397, 398, 399, 421, 424
- hydrogen sulphide 303, 304
- neon 394
- nitrogen 260, 262, 394
- oxygen 292, 424
- sulphur dioxide 289

PALLADIUM ALLOYED WITH COPPER

- hydrogen 301

PALLADIUM ALLOYED WITH GOLD

- hydrogen 261, 288, 301, 397

PALLADIUM ALLOYED WITH PLATINUM

- hydrogen 261, 288, 397

PALLADIUM ALLOYED WITH SILVER

- hydrogen 261, 288, 301, 397

PAPER AND PULP FIBRES

- ammonia 378
- water 379, 387, 388

PARAFFIN

- carbon dioxide 72
- gases 246
- water 246

PENTAACETATE

- water 363

PERMUTIT

- water 193

PLATINUM

- air 264
- alcohol 509
- argon 267
- benzene, 235, 305, 306, 331, 509
- carbon dioxide, 261, 262, 264, 265, 267, 277, 278, 279, 280, 307, 311, 399, 422, 501, 502, 503
- carbon dioxide and hydrogen, 280
- carbon disulphide, 504
- carbon monoxide, 10, 267, 277, 278, 279, 280, 281, 282, 311, 313, 397, 422, 423, 501, 502, 503
- ethylene 311, 509
- helium 283
- hexamethylene 509
- hydrogen, 102, 103, 260, 261, 262, 264, 265, 266, 267, 277, 278, 279, 280, 281, 282, 287, 294, 307, 311, 313, 323, 396, 397, 399, 407, 422, 423, 424, 500

PLATINUM (*contd.*)

hydrogen and carbon dioxide
280

hydrogen and nitrogen 282

hydrogen and oxygen 267, 282

nitrogen 102, 103, 265, 267, 277,
278, 279, 396, 399

nitrogen and hydrogen 282

nitrogen and oxygen 282

oxygen 43, 260, 267, 277, 278,
279, 280, 281, 282, 397, 422,

423, 424, 500, 501, 502, 503

oxygen and hydrogen 267, 282

oxygen and nitrogen 282

oxygen, sulphur trioxide and
sulphur dioxide 305

sulphur dioxide 114, 261, 262,
279, 282, 422, 423

sulphur dioxide, oxygen and
sulphur trioxide 305

sulphur trioxide, oxygen and
sulphur dioxide 305

water 145, 146, 225, 227, 267,
276, 277, 305, 306, 331, 422,
423, 509

PLATINUM, AMALGAMATED

benzene 306, 331

water 306, 331

POTASSIUM BROMIDE

water 246

POTASSIUM CHLORATE

gases 246

water 246

POTASSIUM CHLORIDE

argon 518, 519

POTATO

air 377

carbon dioxide 377

nitrogen 377

oxygen 377

PRASEODYMIUM

hydrogen 260, 261, 287, 293

PROTEINS

acid 382

ammonia 383

hydrogen chloride 383

PUMICE

gases 246

hydrogen 102, 103

nitrogen 102, 103

sulphur dioxide 114

water 179, 246

QUARTZ

alkali hydroxides 330

alkaline earth hydroxides 330

ammonia 247

barium chloride 330

carbon dioxide 247

water 211, 246, 247, 248, 249,
250, 442

RARE EARTH METALS

hydrogen 262

RHODIUM

carbon dioxide 261, 262

hydrogen 261, 262, 285, 287, 294

nitrogen 262

RUBBER

air 384

ammonia 384

benzene 385

benzine 385

carbon dioxide 384

gases 384, 385

hydrogen 384

nitric oxide 384

oxygen 384, 385

sulphur dioxide 114, 384

water 384, 385, 387, 388

RUTHENIUM

carbon dioxide 283

hydrogen 283, 284, 285, 294

SAMARIUM

hydrogen 287

SAND

ammonia 247

carbon dioxide 247

pyridine 233

toluol 233

water 211, 213, 233, 247

SANDSTONE

water 211

SANDSTONES AND THEIR INTER-

GRAIN CEMENT

benzene 211

chloroform 211

ethyl alcohol 211

methyl alcohol 211

octane 211

SAPPHIRE

ammonia 256

SAWDUST

gases, asphyxiating 14

SILICA

acetic acid 200, 392, 393

acetic acid and benzene 392,
393acetone 138, 178, 187, 200, 393,
425

acetylene tetrabromide 187

air 193

alcohol 187, 188, 200, 393, 394,
425, 434, 441

alcohol and ether 200

ammonia 56, 181, 185, 194, 197,
199, 204, 405argon 56, 158, 159, 194, 195,
196, 405benzene 138, 178, 181, 185, 187,
188, 189, 200, 204, 345, 393,
434, 441

benzene and butyl alcohol, 200

benzene and acetic acid 392, 393

benzene and water 178

bromine 194

butane 185, 194, 197, 198, 204

butyl alcohol and benzene 200

carbon dioxide 40, 56, 185, 194,
195, 196, 198, 199, 209, 405,
417, 444carbon dioxide and carbon mon-
oxide 200

carbon dioxide and oxygen 200

carbon monoxide 56, 209

carbon monoxide and carbon
dioxide 200SILICA (*contd.*)carbon monoxide and oxygen
200carbon tetrachloride 179, 200,
345, 393

chlorine 181, 199, 204, 405

chloroform 187, 345, 393

ethane 56

ether 178, 200, 393

ether and alcohol 200

ethyl acetate 200

ethyl alcohol 200

ethylene 56, 195, 405

formic acid 187

gasoline 178

hexane 393

hydrocarbons 197

hydrogen 56, 79, 108, 179, 209

iodine 201

methane 56

methyl acetate 138, 200

methyl alcohol 200

methyl chloride 204

methyl ethyl ketone 138, 200

methyl propionate 200

methylene blue 192

nitric acid 187

nitric oxide 185

nitrobenzene 345

nitrogen 56, 79, 108, 179, 193,
195, 405

nitrogen peroxide 200

nitrous oxide 196, 197, 444

noble gases 193

organic vapours 178

oxides of nitrogen 196

oxygen 108, 193, 195, 209, 405

oxygen and carbon dioxide 200

oxygen and carbon monoxide
200

ozone 195, 405

radium emanation 193

sulphur dioxide 178, 185, 194,
195, 204, 414, 434, 435, 438

sulphuric acid 187

toluene 200

SILICA (*contd.*)

water, 8, 145, 146, 178, 181, 182,
183, 184, 185, 187, 188, 191,
192, 193, 200, 223, 345, 387,
389, 394, 413, 414, 423, 425,
432, 434, 441
water and benzene 178

SILICA AND CARBON (CARBO-GEL)

ammonia 181
benzene 181
chlorine 181
toluene 181
water 181

SILICA, FUSED

air 218
ammonium bromide 235
benzene 193, 235
chlorides 328
helium 193, 213
hydrogen 213, 218, 235
nitrates 328
nitrobenzene 328, 329
nitrogen 213
sodium chloride 328
sulphates 328
sulphur vapour 242
water 193, 211, 225, 227, 230

SILICA GELS, METALLIZED

carbon dioxide 181
carbon monoxide 181
ethylene and methane 181
hydrogen 181
hydrogen sulphide 181
methane and ethylene 181
oxygen 181

SILK

alcohol 382
ammonia 382
carbon dioxide 382
carbon monoxide 382
hydrogen 382
hydrogen chloride 382
hydrogen sulphide 382
nitrogen 382
picric acid 4
sulphur dioxide 382

SILK (*contd.*)

water 378, 379, 380, 381, 382,
388, 425

SILK, ARTIFICIAL

methylene blue B extra 336
water 381, 382, 387, 388

SIL-O-CEL

carbon tetrachloride 178, 179

SILVER

air 265
ammonia 310
argon 267
bromine 307
carbon dioxide 267, 310
carbon monoxide 267
chlorine 307
ethyl violet 336
hydrogen 260, 261, 262, 265,
266, 267, 287, 307, 308, 309,
310, 323
hydrogen and oxygen 267
hydrogen sulphide 307
iodine 307
nitric acid 307
nitrogen 260, 261, 262, 265, 267
oxygen 260, 261, 262, 263, 264,
265, 266, 267
oxygen and hydrogen 267
potassium chloride 332
silver nitrate 332
water 265, 267

SILVER ALLOYED WITH GOLD

oxygen 261

SILVER, AMALGAMATED

water 306, 331

SILVER BROMIDE

orthochrome T-bromide 340
silver nitrate 330

SNOW

gases, asphyxiating 14

SOAP

water 387, 388

SODA LIME

water 389

SODIUM

ammonia 316

SODIUM (*contd.*)

hydrogen 321

SODIUM CHLORIDE

air 329

ammonia 256

carbon dioxide 254, 255, 256

carbon monoxide 254, 255

ethane 256, 257

gases 246

hydrogen 254, 255, 256

methane 254, 256, 257

nitric oxide 255

nitrogen 254, 255, 256

nitrous oxide 256, 257, 329

oxygen 255, 256

propane 256, 257, 329

sulphur dioxide 256, 257, 329

water 246, 252, 253, 254, 256,
329

SODIUM FLUORIDE

neon 519

SODIUM SULPHATE

gases 246

water 246

SOIL

gases, asphyxiating 14

potassium compounds 14

STANNIC ACID

litmus 3

sulphindigodate 3

STANNIC OXIDE

ammonia 205

argon 159

water 192, 194

STANNOUS OXIDE

acetylene 205, 206

ethane 206

ethylenic 206

hydrogen 205, 206

STARCH

air 377

ammonia 377

carbon dioxide 377

hydrogen 377

hydrogen chloride 377

iodine 4, 6

STARCH (*contd.*)

nitrogen 377

oxygen 377

sodium chloride 360

sodium tungstate 360

sulphur dioxide 377

water 376, 388

STEEL

carbon monoxide 265

hydrogen 265

nitrogen 265

STRAW

gases, asphyxiating 14

STRONTIUM SULPHATE

thorium B 334

thorium X 334

SUGAR

air 258

carbon dioxide 72

SULPHUR

litmus 3

sodium chloride 330

sulphindigodate 3

TALC

acetic acid 393

acetone 393

alcohol 393

benzene 393

carbon tetrachloride 393

chloroform 393

ether 393

hexane 393

TANTALUM

argon 260, 262

helium 260, 262

hydrogen 260, 266, 287, 293,

294, 396

nitrogen 260

TEXTILES

dissolved substances 8

water 387

THALLIUM

hydrogen 260, 262, 287

nitrogen 260, 262

THORIA

acetic acid 203, 205
alcohol 205, 208, 411
ethyl acetate 203, 205
ethyl alcohol 203
ethylene 205
hydrogen 205
nitrogen 205
radium emanation 203
thorium emanation 203
water 203, 205, 207

THORIA AND NICKEL

carbon dioxide 311
hydrogen 311
nitrogen 311

THORIUM

hydrogen 261, 287, 293, 294
oxygen 428

TIN

hydrogen 260, 262, 287
nitrogen 260, 262

TIN AND MERCURY

methyl alcohol 395
water 395

TITANIA

acetic acid 205
acetic anhydride 205
acetone 205
ammonia 204, 205
benzene 205
butane 204
carbon dioxide 199, 204
carbon disulphide 205
chlorine 204
chloroform 205
cresol 205
ethane 204
ethyl ether 205
ethylene 204
hydrogen 204
methyl chloride 204
pyridine 205
sulphur dioxide 204
xylene 205

TITANIUM

hydrogen 261, 293, 294, 303

TITANIUM AND VANADIUM SERIES

hydrogen 262

TOBACCO

water 387, 388

TUNGSTEN

barium 269, 525
carbon 269
carbon monoxide 480
caesium 268, 269, 357, 401, 494
hydrogen 260, 262, 287
nitrogen 260, 269, 285
oxygen 12, 43, 269, 401, 479, 480
rare earth metals 269
thorium 268, 269, 428
water 269

TUNGSTEN (OXIDIZED)

caesium 268, 269

TUNGSTEN (THORIUM-COATED)

caesium 268

TUNGSTIC OXIDE

acetic acid 205
alcohol 205, 208
ethyl acetate 205
water 205, 207

URANIUM

argon 260, 262
helium 260, 262
hydrogen 260, 262, 287

VANADIUM

hydrogen 261, 287, 293, 294

VANADIUM ALLOYED WITH IRON

hydrogen 261

VANADIUM AND TITANIUM SERIES

hydrogen 262

VANADIUM OXIDE

carbon dioxide 209
carbon monoxide 209
hydrogen 209
oxygen 209

WOOD

air 377
ammonia 378

WOOD (*contd.*)

- carbon dioxide 72, 119, 377
- gases 2
- hydrogen 370, 371
- nitrogen 370, 371, 377
- oxygen 370, 371, 377
- water 370, 379, 387, 388

WOOL

- acid 382
- ammonia 378
- chlorine 381
- ethylene glycol 396
- fogs 358
- methyl alcohol 378, 396
- methylene glycol 378
- octyl alcohol 378
- propyl alcohol 396
- smokes 358
- sulphur dioxide 381
- water 378, 379, 380, 381, 382, 388, 425

YTTRIUM

- hydrogen 287

ZEOLITES (see also *Analcite, Chabasite, Heulandite*)

- air 169
- ammonia 169
- bromine 169
- calomel 169
- iodine 169
- mercury 169

ZEOLITES (*contd.*)

- water 171

ZINC

- hydrogen 262, 264, 287, 307
- nitrogen 262

ZINC AND BISMUTH

- methyl alcohol 395
- water 395

ZINC OXIDE

- ammonia 411
- benzene 411
- carbon dioxide 207, 208, 411
- carbon monoxide 10, 207
- ethylene 207
- hydrogen 10, 207, 208
- litmus 3
- pyridine 411
- sulphindigodate 3
- sulphur dioxide 411
- water 207, 389, 411
- xylene 411

ZINC OXIDE AND CHROMIC OXIDE

- hydrogen 208, 411

ZIRCONIA

- alcohol 208
- carbon dioxide 199
- radium emanation 203
- thorium emanation 203
- water 203, 207

ZIRCONIC ACID

- water 192

ZIRCONIUM

- hydrogen 261, 287, 293, 294, 322

SUBJECT INDEX

- Absorption 6, 7, 8, 44, 45, 383
 Activation of charcoal 46, 53, 58-79
 — of desorbed gases 44, 265-70
 — of sorption 9, 10, 43, 69, 121, 278, 310-16, 320, 471, 500, 507, 508, 523
 Active patches (see also *Edges*) 496, 503-10
 Adhesion of particles to walls 232, 233
 — tension 149, 345, 346
 Adlineation 506, 507
 Adsorption 7, 45
 — potential 56, 245, 346, 412, 451, 452-8
 Aerogels, expanded 180
 Anisotropy of sorbed material 175
 Area of sorbing surface 13, 138, 170, 224, 325-51, 446
 Atomic distances 81, 82, 83

 Boiling-points and sorption 2, 42, 44, 54, 55, 56, 99, 100, 101, 102, 135, 143, 156
 Breaks or bends (see *Isotherms*)

 Capillary condensation 28, 137, 139, 147, 148, 165, 193, 237, 248, 253, 331, 343, 344, 373, 391, 410, 427, 432-46
 Carboraffin 60, 76, 77, 86, 88
 Catalysis 498-510
 Catalysts, roughening, disintegration (see *Expansion due to sorption*, also pages 394 and 506)
 Cellulose, X-ray structure 82, 359-62, 371

 Characteristic curve of adsorption 453-7
 Charcoal, composition of 69, 70, 75, 77, 78, 88, 93, 117, 122
 —, electrical conductivity of 59, 60
 —, microscopic structure 72
 —, oxidation of (see also *Activation of charcoal*) 3, 8, 9, 44, 64, 69, 121, 122, 123, 193, 407, 419-21, 440
 —, testing of activity 62, 63, 64, 73, 74, 75
 —, X-ray structure of 67, 80, 81
 Chemosorption 9, 10, 12, 14, 45, 46, 69, 70, 71, 72, 82, 114, 120, 185, 186, 187, 199, 243, 271, 272, 278, 281, 282, 284, 296, 315, 360-5, 385, 392, 409, 410, 411, 419-21, 423, 440, 462, 472, 473, 475, 479, 480, 481, 500
 Clean surfaces (see *Evacuation, influence and importance*)
 Clean-up 215-18, 285, 286, 307, 479
 Coherer Method 25, 276, 421, 481
 Combustion, spontaneous 15, 70, 309, 319
 Compressed film hypothesis 3, 36, 165, 427, 428, 447-63, 496, 497
 Compressibility 87, 89, 92, 140, 409, 410
 Condensability and sorption of gases and vapours 2, 42, 44, 54, 55, 56, 143, 157
 Cotton (see *Cellulose*)
 Cracks, surface 329, 330, 333
 Critical pressure of adsorption 149, 482, 483

- Critical temperatures and sorption
2, 42, 44, 54, 55, 56, 102, 109,
111, 112, 172, 180, 346, 440, 444,
452
— temperature of adsorption
522, 524
— — of reflection 149, 482, 483
- Decolorizing 3, 16, 61
- Density, definition of 79, 80
— of charcoal 18, 46, 51, 60, 63,
68, 69, 74, 75, 76, 78, 79-92
— of silica gel 179, 180, 201
- Deodorizing 3, 16
- Diffusion 8, 45, 46, 65, 213-19,
260-5, 283, 295, 298, 306, 354,
355, 384, 386, 397
— in sorbed layers 354, 355
- Dipoles 495, 496, 512-27
- Dyes, sorption of 42, 62, 72, 75,
77, 177, 192, 237, 328, 334-40,
347, 354
- Edges 307, 329, 330, 485, 507
- Electrical resistance, changes in
due to sorption 218, 219, 393,
396, 399
- Electrification of desorbed gases
44, 265-70
- Equation of state for film 357,
493-5, 497, 526
- Evacuation, influence and import-
ance 27, 45, 52, 53, 54, 64, 92-5,
117, 128, 132, 134, 137, 138, 143,
148, 159, 164, 172, 184, 185, 222,
241, 255, 265, 316, 321, 364, 401,
416, 434, 438
- Expansion due to sorption 142,
148, 154, 211, 263, 264, 278, 291,
292, 298, 302, 305, 344, 358, 360,
362, 364, 373, 383, 390-9, 439
- Exponential formula (see *Iso-
therm, classical formula*)
- Fontana experiment 1, 17, 107,
160, 161
- Formulae, bibliography of 485
- Free energy of sorption 35, 411,
484, 521
- Freundlich exponential isotherm
(see *Classical sorption isotherm*)
- Gas Warfare 6, 13, 14, 25, 58, 61,
160, 178
- Getters 216, 218
- Glass, drying of 51, 213-19, 221-3,
236, 238, 239, 242, 245
—, electrolysis through 216, 217
—, sorption by 211-45
- Hardy's experiments 350, 428, 466,
497, 511
- Heat of condensation (see *Heat of
sorption*)
— of sorption 2, 9, 98, 100, 135,
137, 141, 142, 147, 152, 155, 171,
172, 199, 223, 265, 279, 282,
296, 346, 376, 379, 400-25, 438,
463, 470, 507, 508, 522, 524, 526
— of sublimation 413
- Henry's Law 4, 11, 32, 33, 37, 38,
39, 40, 41, 57, 118, 124, 147, 172,
196, 197, 198, 199, 205, 239, 321,
384, 524
- Hydrogels, X-ray structure 186,
203
- Hysteresis 145, 148, 150, 151, 152,
159, 172, 183, 184, 185, 187, 188,
190, 191, 192, 365-9, 443
- Insorption 7
- Interference colours 342-4
- Iodine value 61, 77, 178
- Isobars 40, 96, 97, 99, 100, 102,
103, 158, 171, 293, 294, 307, 308,
313
- Isosteres 40, 41, 100, 116, 125, 131,
132, 133, 141, 142, 155, 400, 491,
493
- Isotherm, classical formula 5, 11,
14, 28, 29, 30, 33, 95, 132, 158,
241, 243

- Isotherms 11, 94
 —, breaks in 153, 172, 174, 175,
 347, 348, 373, 469, 495
 Jellies, structure of 180-94
 Langmuir isotherm 5, 31, 36, 252,
 372, 373, 378, 430, 459, 467-78,
 482-7, 493, 494, 495, 497, 527
 Lecture demonstrations 1, 9, 47,
 157, 282, 397 (see Dewar's
 papers)
 Luminescence 93
 Mass law and sorption 4
 McBain-Bakr sorption balance 20,
 128, 363
 McBain-Tanner sorption balance
 23
 Magnetic susceptibility of charcoal
 67, 175, 288, 300, 301
 Measurement of sorption, Chap. II
 17-28
 Method of McHaffie and Lenher
 224-31, 234, 235, 236, 305, 306,
 327
 Methods, dynamic 25
 Methylene blue (see *Dyes*)
 Mixtures, sorption of 24, 52,
 159-66, 172, 200, 303, 304, 319,
 351
 Mobility in sorbed films 352-7,
 383, 429, 430
 Mohamet's coffin 350
 Moisture regain 362, 371, 378-82,
 387-9
 Molecular sieve 92, 169, 173, 177,
 292, 336, 358, 378, 396
 Monomolecular layers 325-51, 428,
 464-97, 498-510
 Multimolecular layers 325-33,
 348-51, 428, 495-7
 Multiple absorption 472, 488, 489,
 508-10
 Mutual polarization of sorbed
 molecules 149, 482, 524, 525
 Norit 58, 64, 73, 76, 77, 87
 Occlusion = Sorption 1, 45, 259-
 65
 Optical method 26, 231, 253, 270,
 329
 Orientation in sorbed layers 175
 Palladium hydride 288, 301
 Persorption 13, 14, 46, 64, 73, 80,
 81, 82, 95, 108, 118, 146, 148,
 169, 170, 171, 177, 346, 347,
 355, 383, 486
 Photoelectricity 323, 392
 Photography 53, 54
 Polányi hypothesis (see *Compressed
 film hypothesis*)
 Polarization during electrolysis
 340-2
 Polar molecules 130, 131
 Pore, Zsigmondy's term 182, 187,
 441
 Powdering, effect of 65
 Pressure, influence of 6, 35, 96,
 107-13, 459-61
 Promoters 508-10
 Proteins, X-ray structure of 382
 Radioactive solutions, sorption
 from 333, 334
 Range of molecular attraction 325,
 326, 348-51, 427-30, 447-63,
 465, 466, 489, 491, 492, 496,
 511
 Rate of sorption (see also *Time,
 influence of*) 47, 48, 49, 50, 51,
 52, 53, 54, 134, 151, 160, 172,
 174, 200, 246, 304, 364, 381
 Rate of spreading 354, 355
 Ratios between amounts sorbed
 10, 15, 102, 103, 104, 105, 139,
 140, 141, 143, 157, 158, 160, 161,
 173, 179, 233, 280, 307, 311, 317
 Reflection of electrons 321-4, 487
 — of incident molecules 149, 235,
 352, 465-70, 482, 483

- Reichinstein's displacement principle 166, 349
- Relative humidity = relative pressure 39, 125, 143
- Retentivity = prehensibility 63, 64, 74, 75, 177, 178, 179, 192, 197, 203, 221, 411, 422
- Reversible equilibrium 7, 9, 10, 28, 43, 69, 121, 152, 160, 172, 183, 185, 188, 198, 278, 282, 372, 375, 406
- Rubber, X-ray structure of 383, 384, 392
- Saturation value 94, 110, 111, 113, 129, 130, 131, 146, 147, 203, 204, 252, 281, 309, 319, 486, 491
- Siloxene 175, 176
- Solid solution 6, 8, 44, 46, 170, 171, 213-20, 240, 254, 259-65, 291, 297, 383
- Solubility, its parallelism with sorption 57, 241, 377, 384
- Solutions, sorption from 14, 27, 42, 62, 63, 328, 329, 330, 332, 333-40
- Sorbed layers, X-ray structure of 67, 322, 354, 360, 439
- Sorption 1, 6, 7, 8, 44, 45, 46, 47
- balances 19, 23
- pipette 24, 368-70
- Specific heat of sorbed material 174, 223, 299, 300
- Statistical theory 482-4, 493, 527
- Steric hindrance 41, 42, 140, 141, 142, 400, 486
- Swelling 358
- Temperature, influence of 9, 10, 11, 12, 42, 51, 59, 68, 70, 96, 103, 124, 125, 141, 143, 147, 261-4, 278, 279, 282, 290, 298, 310-14, 316, 320, 321, 372, 374, 375, 376, 486-8, 493, 507, 508
- Temperatures, low, produced by sorption 400
- Thermionic emission 268, 269, 479
- Thickness of sorbed layer 203, 222, 223, 225, 227-31, 233-7, 240-3, 245, 247-53, 256, 258, 261, 265, 270-8, 282, 305, 306, 325-51, 427-30
- Time, influence of 3, 7, 44, 45, 46, 47, 59, 121, 134, 135, 191, 208, 231, 269, 280, 298, 372, 392
- Ultrafiltration (see *Molecular sieves*)
- Ultrapores 46, 78, 80, 81, 90, 92, 94, 103, 140, 169, 170
- Umschlagspunkt, Zsigmondy's term 183, 434
- Vacua, influence of sorbed material 214-19, 260, 285
- , production by sorption 10, 15
- van der Waals constant a 54, 55, 89, 447, 451, 456-8, 461, 490, 491, 514, 516, 520, 522
- Vapours, sorption of 125-54, 437
- Wetting 53, 63, 77, 144, 148, 275, 276, 344-7, 406, 411, 415, 416, 423-5, 435, 444
- Williams-Henry isotherm 32, 346, 347, 489-93
- Wool, X-ray structure of 377, 378
- X-ray structure (see *Cellulose, Charcoal, Hydrogels, Proteins, Rubber, Sorbed layers, Wool, Zeolites*, and also pages 359 and 390)
- — of copper 317
- — of palladium 301, 302, 398
- — of platinum 278, 397
- Zeolites, structure of 167, 168, 169

